Lecture notes for the course

554017 ADVANCED QUANTUM CHEMISTRY

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Contents

Chapter 1

Many-electron quantum mechanics

1.1 Molecular Schrödinger equation

The *Schrödinger equation* for a quantum system of N electrons and K nuclei – a molecule – is[1]

$$\hat{H}\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N; \mathbf{X}_1, \mathbf{X}_2, \ldots, \mathbf{X}_K; t) = i\frac{\partial}{\partial t}\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N; \mathbf{X}_1, \mathbf{X}_2, \ldots, \mathbf{X}_K; t) \quad (1.1)$$

The wave functions Ψ describe all the chemical and physical properties of the system; subject only to limitations in the Hamiltonian $\hat{H}$ and the approximations made in the solution of this equation. The variables $\{\mathbf{x}\}$ and $\{\mathbf{X}\}$ are used to collectively symbolize all variables needed to describe the electrons and nuclei; here the position in space and the internal degree of freedom, *spin* (see Section 1.2).

1.1.1 Molecular Hamiltonian

In (1.1), $\hat{H}$ is the *molecular Hamiltonian*, which is for a molecule containing N electrons and M nuclei with charges $\{Z_K\}(K = 1, \ldots, M)$ [1–3]

$$\hat{H} = \hat{H}_e + \hat{H}_n + \hat{H}_{en} \quad (1.2)$$

$$\hat{H}_e = -\frac{1}{2}\sum_{i=1}^{N}\nabla^2 + \sum_{i=1}^{N}\sum_{j=i+1}^{N}\hat{|}\mathbf{r}_i - \mathbf{r}_j|^{-1} \quad (1.3)$$

$$\hat{H}_n = -\frac{1}{2}\sum_{K=1}^{M}\frac{1}{m_K}\nabla_K^2 + \sum_{K=1}^{M}\sum_{L=K+1}^{M}\frac{Z_K Z_L}{|\mathbf{R}_K - \mathbf{R}_L|} \quad (1.4)$$

$$\hat{H}_{en} = -\sum_{K=1}^{M}\sum_{i=1}^{N}\frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_K|}. \quad (1.5)$$

[1] In atomic units used throughout this course, where $\hbar = m_e = 4\pi\epsilon_0 = e =\equiv 1$; $c = 1/\alpha \approx 137$.

The wave function is correspondingly dependent on both the electron and nuclear variables. Usually, because of the large ratio m_n/m_e, it is a good approximation to treat the nuclei fixed in space. This will decouple the electronic and nuclear degrees of freedom, and we may turn our attention to the electronic problem. This is referred to as the *Born–Oppenheimer approximation*. Consequently, the first term in (1.5) vanishes and its second will not affect the solution of the electronic Schrödinger equation. The result is the standard framework in quantum chemistry, *molecular electronic Hamiltonian*,

$$\hat{H} = \sum_{i=1}^{N} \hat{h}_i + \sum_{i=1}^{N} \sum_{j=i+1}^{N} \hat{g}_{ij} \tag{1.6}$$

where $\hat{h}_i$ is the one-electron Hamiltonian of electron i moving in an electrostatic potential caused by the nuclei, and $\hat{g}_{ij}$ is the interaction between the electrons i and j:

$$\hat{h}_i = -\frac{1}{2}\nabla_i^2 - \sum_{K=1}^{M} \frac{Z_K}{|\mathbf{r}_i - \mathbf{R}_K|} \tag{1.7}$$

$$\hat{g}_{ij} = |\mathbf{r}_i - \mathbf{r}_j|^{-1}. \tag{1.8}$$

In the case of fixed nuclei, the contribution from (1.5) reduces to a simple summation,

$$E_{\text{tot}} = E_{\text{electronic}} + \frac{1}{2} \sum_{K=1}^{M} \sum_{L=K+1}^{M} \frac{Z_K Z_L}{|\mathbf{R}_K - \mathbf{R}_L|}. \tag{1.9}$$

1.1.2 Time-independent Schrödinger equation

In quantum chemistry, usually the *time-independent form* of (1.1), with now also invoking the Born–Oppenheimer approximation,

$$\hat{H}\Psi_n(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = E_n \Psi_n(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N), \tag{1.10}$$

is under consideration. The corresponding eigenvalues E_n are in the present context the quantized *energy levels* of the electronic cloud of the molecule. The eigenfunctions or *wave functions* Ψ_n describe the electronic structure and properties of the molecule.

Any two eigenfunctions that correspond to different energy values E_n, E_m possess the *orthogonality property*

$$\int \Psi_n^* \Psi_m d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N = 0. \tag{1.11}$$

Even if two or more eigenvalues happen to be identical, corresponding to a degenerate state of the system, the different eigenfunctions may still be assumed orthogonal.

Furthermore, it is necessary that the wave function is *square-integrable*,

$$\int \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N = a \in \mathbb{R}. \tag{1.12}$$

Usually we also assume that the wave function is normalized, i.e., $a = 1$.

1.1.3 Limitations

Eq. (1.10) provides a basis for molecular quantum mechanics and all the static electronic properties of the molecule may be obtained by expectation values of the appropriate Hermitian operators or using perturbation theory. However, we should recognize the limitations of this model:

- Born–Oppenheimer approximation. The nuclear-motion Hamiltonian (1.2) plays a central role in molecular spectroscopy. The motion of nuclei can sometimes affect even those properties that are considered electronic. This is the case e.g. in the Jahn–Teller effect and the Renner effect.

- Other limitations in the Hamiltonian (1.6): non-relativistic kinematics, instant interactions, point-like nuclei, and electrostatic interactions only. We will address the two first of these in Chapter 7.

- Eq. (1.1) has analytical solutions only for a few trivial one-electron systems, such as hydrogen-like atom or the molecule H_2^+. Therefore we are resorted to make approximate solutions, aiming at systematic and controllable approximations, as we will discuss in later Chapters.

- Real experiments are not carried out for an isolated molecule, and observation always involves *interaction* with the system, and thus a time-independent description is not sufficient; but the time-dependent form (1.1) should be applied. There are also means for treating dynamical effects in the electronic cloud also within the framework of the time-independent eigenvalue equation (1.10) [4]. Addressing these methods is out of the scope of this course.

1.1.4 Example: Helium-like atom

For a helium-like atom with a point-like nucleus of charge Z the electronic Hamiltonian, Eq. (1.6), is

$$\hat{H} = \hat{h}_1 + \hat{h}_2 + \hat{g}_{12} = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_2} + \frac{1}{r_{12}}.$$

Due to $\hat{g}_{12}$, this is a three-body problem, and thereby no closed form solution exists for the eigenvalue equation (1.1). We start our consideration by an approximation, where $\hat{g}_{12}$ is set to zero, i.e. $\hat{H}_0 = \hat{h}_1 + \hat{h}_2$. We can separate the variables in the eigenvalue equation $H_0\Psi_0 = E\Psi_0$ by substituting[2]

$$\Psi_0 = \Phi(\mathbf{r}_1, \mathbf{r}_2) = \chi_1(\mathbf{r}_1)\chi_2(\mathbf{r}_2),$$

[2]Considering only the variables $\mathbf{r}$ (position vectors), which in this case are most conveniently represented as the variables of spherical coordinates, $\mathbf{r} = (r, \theta, \rho)$

to the eigenvalue equation and dividing by Φ, obtaining

$$\frac{\hat{h}_1\chi_1(\mathbf{r}_1)}{\chi_1(\mathbf{r}_1)} + \frac{\hat{h}_2\chi_2(\mathbf{r}_2)}{\chi_2(\mathbf{r}_2)} = E,$$

meaning that Φ is a solution if (denoting $E = \epsilon_1 + \epsilon_2$)

$$\begin{aligned} \hat{h}_1\chi_1(\mathbf{r}_1) &= \epsilon_1\chi_1(\mathbf{r}_1) \\ \hat{h}_2\chi_2(\mathbf{r}_2) &= \epsilon_2\chi_2(\mathbf{r}_2), \end{aligned}$$

meaning that χ_1 and χ_2 are solutions of the one-electron eigenvalue problem $\hat{h}\chi = \epsilon\chi$. Φ is a *simultaneous eigenstate* of the operators $\hat{h}_1$ and $\hat{h}_2$,

$$\begin{aligned} \hat{h}_1\Phi(\mathbf{r}_1,\mathbf{r}_2) &= \epsilon_1\Phi(\mathbf{r}_1,\mathbf{r}_2) \\ \hat{h}_2\Phi(\mathbf{r}_1,\mathbf{r}_2) &= \epsilon_2\Phi(\mathbf{r}_1,\mathbf{r}_2). \end{aligned}$$

The 1-electron 1-center eigenfunctions that are solutions to the one-electron eigenvalue problem (this holds only in the absence of $\hat{g}$) are the same with the solutions of the Schrödinger equation for a hydrogen-like atom (note the factor Z),

$$\chi_{nlm}(r,\theta,\rho) = R_{nl}(r)Y_{lm}(\theta,\rho), \tag{1.13}$$

consisting of the radial part

$$R_{nl}(r) = \left(\frac{2Z}{n}\right)^{3/2}\sqrt{\frac{(n-l-1)!}{2n(n+1)!}}\left(\frac{2Zr}{n}\right)^{l} L_{n-l-1}^{2l+1}\left(\frac{2Zr}{n}\right)\exp\left(-\frac{Zr}{n}\right) \tag{1.14}$$

and a spherical harmonic function, explicitly expressed as

$$Y_{lm}(\theta,\rho) = \sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta)\exp(\mathrm{i}m\rho). \tag{1.15}$$

In the above, L denotes the associated Laguerre polynomials

$$L_n^{\alpha}(x) = \frac{1}{n!}\exp(x)x^{-\alpha}\frac{d^n}{dx^n}\left[\exp(-x)x^{n+\alpha}\right] \tag{1.16}$$

and P the Legendre polynomials

$$P_l^m(x) = \frac{(-1)^m}{2^l l!}(1-x^2)^{m/2}\frac{d^{l+m}}{dx^{l+m}}(x^2-1)^l; \qquad P_l^{-m} = (-1)^m\frac{(l-m)!}{(l+m)!}P_l^m(x). \tag{1.17}$$

1.1.5 Example: Dihydrogen ion

When moving from atoms to molecules, the first complication is that even the *one*-electron eigenfunctions, even when $\hat{g} = 0$, are not obtainable in closed form. Instead of the one-center χ_{nlm} functions (1.13) we need polycentric *molecular orbitals* (MO) that describe the states of a single electron spread around the whole nuclear framework.

The one-electron eigenvalue equation in the case of hydrogen molecule ion H_2^+ is $\hat{h}\phi = \epsilon\phi$, where

$$\hat{h} = -\frac{1}{2}\nabla^2 - \left(\frac{1}{r_A} + \frac{1}{r_B}\right).$$

This may be solved with high accuracy in confocal elliptic coordinates, the solution being a product of three factors that are in turn solutions of three separate differential equations. We will, however, go immediately to approximations. It is reasonable to expect that

$$\begin{aligned} \phi(\mathbf{r}) &\sim c_A\chi^A_{100}(\mathbf{r}) \text{ (densities close to nucleus A)} \\ \phi(\mathbf{r}) &\sim c_B\chi^B_{100}(\mathbf{r}) \text{ (densities close to nucleus B)} \end{aligned}$$

where c_A and c_B are some numerical factors. An appropriate trial MO would then be

$$\phi(\mathbf{r}) = c_A\chi^A_{100}(\mathbf{r}) + c_B\chi^B_{100}(\mathbf{r}).$$

Due to the symmetry of the molecule, it is reasonably to assume that there is no higher density in the other end than in the other; therefore

$$|\phi(\mathbf{r})|^2 = c_A^2[\chi^A_{100}(\mathbf{r})]^2 + c_B^2[\chi^B_{100}(\mathbf{r})]^2 + 2c_Ac_B\chi^A_{100}(\mathbf{r})\chi^B_{100}(\mathbf{r}),$$

implies that $c_B = \pm c_A$. Thus, it appears that we can construct two rudimentary MOs from the $1s$ AOs on the two centers, denoted by

$$\begin{aligned} \phi_1(\mathbf{r}) &= c'_A[\chi^A_{100}(\mathbf{r}) + \chi^B_{100}(\mathbf{r})] \\ \phi_2(\mathbf{r}) &= c'_B[\chi^A_{100}(\mathbf{r}) - \chi^B_{100}(\mathbf{r})], \end{aligned}$$

where the remaining numerical factors c'_A and c'_B are to be chosen so that the wave functions will be normalized.

MOs build up this way, in *linear combination of atomic orbitals* (LCAO), are of great importance throughout molecular quantum mechanics.

1.2 Electron spin and wave function antisymmetricity

1.2.1 Spin functions

It is well-known that a single electron is not completely characterized by its spatial wave function $\phi(\mathbf{r})$, but an intrinsic angular momentum, spin, is required to explain e.g. line emission spectra of atoms in an external magnetic field. Therefore we must introduce a

spin variable σ in addition to $\mathbf{r}$. We further associate operators $\hat{s}_x$, $\hat{s}_y$ and $\hat{s}_z$ with the three components of spin angular momentum. We will adopt $\mathbf{x}$ as a variable taking into account both degrees of freedom, σ and $\mathbf{r}$, and then introduce *spin-orbitals*

$$\psi(\mathbf{x}) = \phi(\mathbf{r})\eta(\sigma). \tag{1.18}$$

η describes the spin state and is a solution of an eigenvalue equation $\hat{s}_z\eta = \lambda\eta$. If the orbital state is of energy ϵ, then

$$\hat{h}\psi = \epsilon\psi \tag{1.19}$$

$$\hat{s}_z\psi = \lambda\psi, \tag{1.20}$$

and ψ is a state in which an electron simultaneously has definite energy and z-component of spin.

In the case of electrons, the eigenvalue equation (1.20) has only two solutions:

$$\hat{s}_z\alpha = \frac{1}{2}\alpha; \qquad \hat{s}_z\beta = -\frac{1}{2}\beta,$$

with the eigenfunctions α and β often referred to as "spin-up" and "spin-down", respectively. Therefore an orbital ϕ yields two possible spin-orbitals, $\psi = \phi\alpha$ and $\psi' = \phi\beta$. These spin functions may be thought as "spikes" at the points $s_z = +1/2$ and $s_z = -1/2$, respectively, and their normalization and orthogonality properties are

$$\int \alpha^*\alpha d\sigma = \int \beta^*\beta d\sigma = 1 \tag{1.21}$$

$$\int \alpha^*\beta d\sigma = \int \beta^*\alpha d\sigma = 0. \tag{1.22}$$

Also the *total spin operators*

$$\hat{S}_z = \sum_{i=1}^{N} \hat{s}_{z,i} \tag{1.23}$$

$$\hat{S}^2 = \sum_{i=1}^{N} \hat{s}_i^2 = \sum_{i=1}^{N} \left(\hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2\right) \tag{1.24}$$

with eigenvalues of M and $S(S+1)$, respectively, are needed in the discussion of many-electron system. They commute with a spin-free electronic Hamiltonian; and any exact stationary state Ψ is an eigenfunction of them.

1.2.2 Antisymmetry principle

The fact that electrons are indistinguishable, i.e. $|\Psi(\mathbf{x}_1, \mathbf{x}_2)|^2 = |\Psi(\mathbf{x}_2, \mathbf{x}_1)|^2$, leads to (when generalized for N-electrons) two possibilities for a wave function:

$$\hat{P}\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \qquad \text{symmetric wave function}$$

$$\hat{P}\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \varepsilon_P\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \qquad \text{antisymmetric wave function}$$

where the operator $\hat{P}$ permutes the arguments and ε_P is $+1$ for an even and -1 for an odd number of permutations.

The choice for an system consisting of N *electrons* is once and for all determined by the *antisymmetry principle* (Pauli exclusion principle):

The wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$ that describes any state of an N-electron system is *antisymmetric* under any permutation of the electrons.

1.2.3 Example: Spin orbitals of $1s^2$ state of He

When spin is included, the electrons must each be assigned to *spin-orbitals* $1s\alpha$, $1s\beta$, $2s\alpha, \ldots$ For the $1s^2$ configuration, both electrons may occupy the $1s$ orbital with the following choices of spin variables:

$$\begin{aligned}
\Phi_1(\mathbf{x}_1, \mathbf{x}_2) &= \chi_{100}(\mathbf{r}_1)\alpha(s_1)\chi_{100}(\mathbf{r}_2)\alpha(s_2) \\
\Phi_2(\mathbf{x}_1, \mathbf{x}_2) &= \chi_{100}(\mathbf{r}_1)\beta(s_1)\chi_{100}(\mathbf{r}_2)\beta(s_2) \\
\Phi_3(\mathbf{x}_1, \mathbf{x}_2) &= \chi_{100}(\mathbf{r}_1)\alpha(s_1)\chi_{100}(\mathbf{r}_2)\beta(s_2) \\
\Phi_4(\mathbf{x}_1, \mathbf{x}_2) &= \chi_{100}(\mathbf{r}_1)\beta(s_1)\chi_{100}(\mathbf{r}_2)\alpha(s_2).
\end{aligned}$$

All of these functions have the same eigenvalue $E = 2\epsilon_{1s}$ of the electronic Hamiltonian.

It is apparent that Φ_1 and Φ_2 are symmetric under interchange of $\mathbf{x}_1$ and $\mathbf{x}_2$, and are thus non-suitable to describe the electrons. However, we may form *linear combinations* of Φ's to obtain the desired behavior under the interchange. For instance, the following appears to be acceptable:

$$\Psi_1(\mathbf{x}_1, \mathbf{x}_2) = [\Phi_3(\mathbf{x}_1, \mathbf{x}_2) - \Phi_4(\mathbf{x}_1, \mathbf{x}_2)]/\sqrt{2}$$

1.2.4 The Slater determinant

The previous argumentation may be directly generalized for any N-electron wave function. For more than two electrons, a large number of differently permuted product functions must be combined to yield a fully antisymmetric wave function.

Expanded in particular permutations κ the exact wave function[3] is written as

$$\begin{aligned}
\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) &= \sum_\kappa c_\kappa \Phi_\kappa(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) && (1.25) \\
&= \sum_\kappa c_\kappa M_\kappa \left[\sum_P \varepsilon_P \hat{P} \psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\cdots\psi_n(\mathbf{x}_N) \right]. && (1.26)
\end{aligned}$$

M_κ are normalization coefficients and Φ_κ is most conveniently expressed as a *Slater determinant*

$$\Phi_\kappa(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = M \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_2(\mathbf{x}_1) & \cdots & \psi_n(\mathbf{x}_1) \\ \psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) & \cdots & \psi_n(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\mathbf{x}_N) & \psi_2(\mathbf{x}_N) & \cdots & \psi_n(\mathbf{x}_N) \end{vmatrix}. \qquad (1.27)$$

[3]Exact at the limit $\kappa \to \infty$

Combinations which are symmetric under variable permutations are automatically rejected by the Slater determinant, and thus the Pauli principle is fulfilled.

The normalization factor M is reasoned in the following way: when expanded, Φ consists of $N!$ products, and thus an integrand $\Phi^*\Phi$ would consist of $(N!)^2$ products, each of a form

$$\pm[\psi_1(\mathbf{x}_i)\psi_2(\mathbf{x}_j)\cdots\psi_n(\mathbf{x}_k)][\psi_1(\mathbf{x}_{i'})\psi_2(\mathbf{x}_{j'})\cdots\psi_n(\mathbf{x}_{k'})].$$

It is evident that unless $i = i'$, $j = j'$ etc. in a particular product, the product will give no contribution to the result, due to the orthogonality of spin-orbitals. Therefore, there is $N!$ non-vanishing contributions, and as every contribution is equal to 1 with normalized spin-orbitals, we have $\int \Phi^*\Phi d\mathbf{x}_1\cdots d\mathbf{x}_N = M^2N!$, hence the normalization factor has the value $M = (N!)^{-1/2}$.

1.2.5 Example: Approximate wave functions for He as Slater determinants

The Slater determinant of the configuration $(1s)^2$ of a helium atom in the minimal orbital basis is

$$\Psi_1 = \frac{1}{\sqrt{2}}\begin{vmatrix} \chi_{100}(\mathbf{r}_1)\alpha(\sigma_1) & \chi_{100}(\mathbf{r}_1)\beta(\sigma_1) \\ \chi_{100}(\mathbf{r}_2)\alpha(\sigma_2) & \chi_{100}(\mathbf{r}_2)\beta(\sigma_2) \end{vmatrix} \equiv \frac{1}{\sqrt{2}}\det|1s\alpha\ 1s\beta|.$$

Note the abbreviated notation that will be used quite extensively hereafter: only the diagonal elements are displayed, and the explicit expression of variables is omitted – the left-right order of the variables in this notation will be $1, 2, 3, \ldots$. Also, note that we have denoted χ_{nlm}'s with their corresponding AO labels.

Respectively, the proper antisymmetric wave functions for the excited 1s2s configuration are written as

$$\begin{aligned}
\Psi_2 &= \frac{1}{\sqrt{2}}\det|1s\alpha\ 2s\alpha| \\
\Psi_3 &= \frac{1}{2}\left(\det|1s\alpha\ 2s\beta| + \det|1s\beta\ 2s\alpha|\right) \\
\Psi_4 &= \frac{1}{\sqrt{2}}\det|1s\beta\ 2s\beta| \\
\Psi_5 &= \frac{1}{2}\left(\det|1s\alpha\ 2s\beta| - \det|1s\beta\ 2s\alpha|\right).
\end{aligned}$$

1.2.6 Example: Helium-like atom revisited

Consider the 2-electron Hamiltonian, now including electron-electron interaction, $\hat{H} = \hat{h}_1 + \hat{h}_2 + \hat{g}$. Let us assume that the (normalized) wave function Ψ_1 approximates the $(1s)^2$ configuration of the He atom. The corresponding energy is obtained as an expectation value $H_{11} = \left\langle \Psi_1 \middle| \hat{H} \middle| \Psi_1 \right\rangle$. Now

$$H_{11} = \frac{1}{2}\int \{\chi^*_{100}(\mathbf{r}_1)\chi_{100}(\mathbf{r}_2)\left[\alpha(\sigma_1)\beta(\sigma_2) - \alpha(\sigma_2)\beta(\sigma_1)\right]^*$$

$$\times \hat{H}\chi_{100}(\mathbf{r}_1)\chi_{100}(\mathbf{r}_2)\left[\alpha(\sigma_1)\beta(\sigma_2) - \alpha(\sigma_2)\beta(\sigma_1)\right]\Big\} d\mathbf{r}_1 d\mathbf{r}_2 d\sigma_1 d\sigma_2,$$

but since the Hamiltonian does not operate on spins, we may perform the spin-integration immediately [c.f. Eq. (1.22)],

$$\int \left[\alpha(\sigma_1)\beta(\sigma_2) - \alpha(\sigma_2)\beta(\sigma_1)\right]^* \left[\alpha(\sigma_1)\beta(\sigma_2) - \alpha(\sigma_2)\beta(\sigma_1)\right] d\sigma_1 d\sigma_2 = 2.$$

Thus we have

$$\begin{aligned}
H_{11} &= \int \chi^*_{100}(\mathbf{r}_1)\chi^*_{100}(\mathbf{r}_2)\hat{H}\chi_{100}(\mathbf{r}_1)\chi_{100}(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 \\
&= \int \chi^*_{100}(\mathbf{r}_1)\hat{h}_1\chi_{100}(\mathbf{r}_1)d\mathbf{r}_1 \int \chi^*_{100}(\mathbf{r}_2)\chi_{100}(\mathbf{r}_2)d\mathbf{r}_2 \\
&\quad + \int \chi^*_{100}(\mathbf{r}_2)\hat{h}_2\chi_{100}(\mathbf{r}_2)d\mathbf{r}_2 \int \chi^*_{100}(\mathbf{r}_1)\chi_{100}(\mathbf{r}_1)d\mathbf{r}_1 \\
&\quad + \int \chi^*_{100}(\mathbf{r}_1)\chi^*_{100}(\mathbf{r}_2)\hat{g}\chi_{100}(\mathbf{r}_1)\chi_{100}(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 \\
&= 2\epsilon_{1s} + J
\end{aligned}$$

This result is still an approximation, with only difference to the independent-particle model being the contribution J from the two-electron integral. The next step in the determination of He energy levels would be to include more and more Slater determinants corresponding to excited state configurations and evaluate the respective matrix elements. As anticipated earlier, although the exact solution would require an infinite number of included determinants, the energy spectrum would in practise converge towards the correct one rather rapidly. However, the analysis of the many-electron problem using this kind of direct expansion would obviously be extremely tedious, and a more general approach is needed. Also, the evaluation of integrals gets far more complicated in the case of many atomic cores.

1.2.7 Slater's rules

We may indeed devise more systematic rules for the matrix elements. We begin by noting that the expectation value over the 1-electron part of the molecular Hamiltonian, $\sum_{i=1}^{N}\hat{h}_i$, will reduce to the sum of N identical terms, since the coordinates of each electron appear symmetrically in the corresponding integral:

$$\left\langle \Phi \left| \sum_i \hat{h}_i \right| \Phi \right\rangle = \sum_r \left\langle \psi_r \left| \hat{h} \right| \psi_r \right\rangle . \tag{1.28}$$

The expectation value of the two-electron part is a bit more complicated, as contributions may arise from terms that differ by an interchange of two electrons; but essentially a

similar argumentation leads to

$$\left\langle \Phi \left| \sum_{ij}{}' \hat{g}_{ij} \right| \Phi \right\rangle = \sum_{rs}{}' \left(\langle \psi_r \psi_s \left| \hat{g} \right| \psi_r \psi_s \rangle - \langle \psi_r \psi_s \left| \hat{g} \right| \psi_s \psi_r \rangle \right), \tag{1.29}$$

where the former part is referred to as the *Coulomb integral* and the latter as the *exchange integral*. the expectation value of the energy being simply the sum of (1.28) and (1.29).

We also need the off-diagonal elements. Fortunately enough, there are non-vanishing elements only in two cases:

- one spin-orbital is different between Φ and Φ' ($\psi'_r \neq \psi_r$) when

$$\left\langle \Phi' \left| \hat{H} \right| \Phi \right\rangle = \left\langle \psi'_r \left| \hat{h} \right| \psi_s \right\rangle + \sum_{s \neq r} \left(\langle \psi'_r \psi_s \left| \hat{g} \right| \psi_r \psi_s \rangle - \langle \psi'_r \psi_s \left| \hat{g} \right| \psi_s \psi_r \rangle \right), \tag{1.30}$$

- two spin-orbitals are different ($\psi'_r \neq \psi_r$, $\psi'_s \neq \psi_s$) when

$$\left\langle \Phi' \left| \hat{H} \right| \Phi \right\rangle = \left(\langle \psi'_r \psi'_s \left| \hat{g} \right| \psi_r \psi_s \rangle - \langle \psi'_r \psi'_s \left| \hat{g} \right| \psi_s \psi_r \rangle \right), \tag{1.31}$$

These results are called *Slater's rules*. In Slater's rules, the spin-orbitals are required to be orthonormal, but the rules may be generalized for matrix elements even in a non-orthogonal spin-orbital basis.

1.3 Concerning interpretation

What is the *physical* meaning of the wave functions introduced earlier? First of all, the general formulation of quantum mechanics is concerned only with symbolic statements involving relationships between operators and operands, and is independent of the employed representation or interpretation.

In a very "orthodox" interpretation, MOs as well as spin-orbitals are just mathematical means for the solution of the molecular Schrödinger equation and no physical meaning can be given for them or even their squared norms.

Perhaps more commonly, a spin-orbital $\psi(\mathbf{x})$ itself is thought to be just a mathematical entity but $|\psi(\mathbf{x})|^2 d\mathbf{x}$ is taken to be the probability of *a point-like electron being in an element* $d\mathbf{x}$, or in volume element $d\mathbf{r}$ with spin between σ and $\sigma + d\sigma$. $|\phi(\mathbf{r})|^2 d\mathbf{r}$ is the probability of finding an electron with any spin in the volume element $d\mathbf{r}$. Also $\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$ cannot be interpreted; but $|\Psi|^2 d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N$ is a probability of the electron 1 in $d\mathbf{x}_1$, electron 2 *simultaneously* in $d\mathbf{x}_2$, etc. Then, the probability of electron 1 being in $d\mathbf{x}_1$ while other electrons are anywhere would be equal to $d\mathbf{x}_1 \int \Psi^* \Psi d\mathbf{x}_2 \cdots d\mathbf{x}_N$.

However, it might be better to think of an electron as being *delocalized*, i.e. not having a more precise position than that indicated by its spatial part of the wave function $\phi(\mathbf{r})$. Then $|\phi(\mathbf{r})|^2 d\mathbf{r}$ would be the amount of charge in an element $d\mathbf{r}$. In other words, in this point

of view a MO can be thought to approximately describe an electron really spread around the nuclear framework. However, as we will see later, MOs can be unitarily "rotated", i.e. their form shaped, and they still correspond to the same definite energy. Which MOs are then closest to the physical ones?

1.4 One- and N-electron expansions

Let us recall: the Slater determinants do not represent an accurate solution to the molecular Schrödinger equation, but we may express the exact wave function as a linear combination of determinants. Furthermore, we have to expand the molecular orbitals in the determinants as a linear combination of atomic orbitals

$$\phi_a = \sum_\mu C_{\mu a} \chi_\mu(\mathbf{r}). \tag{1.32}$$

As we will see later, atomic orbitals are further approximated with a set of simpler functions that are also functions of the coordinates of a single electron. This three-step procedure is often referred to as the "standard model of quantum chemistry".[4] To arrive at the exact solution (within the given Hamiltonian), i) orbitals in terms of which the determinants are constructed must form a complete set in one-electron space, and ii) in the expansion of N-electron wave function, we must include all determinants that can be generated from these orbitals.[5]

All approximations in the solution of the Schrödinger equation should be unambigious and precisely defined. Ideally, they should be improvable in a systematic fashion; and to yield more and more elaborate solutions that approach the exact solution. Thus we speak of different *models*, *levels of theory* and *hierarchies of approximations*.

Computational electronic-structure theory has a few *standard models* for the construction of approximate electronic wave functions. At the simplest level, the wave function is represented by a single Slater determinant (the Hartree–Fock approximation); and at the most complex level the wave function is represented as a variationally determined superposition of all determinants in the N-electron Fock space (full configuration-interaction, FCI). Between these extremes, there are a vast number of intermediate models with variable cost and accuracy. These will be discussed in Chapters

It should be noted that none of the models is applicable to all systems. However, each model is applicable in a broad range of molecular systems, providing solutions of known quality and flexibility at a given computational cost.

Furthermore, there are in fact *three* general features determining the accuracy of quantum chemical methods:[6] electron correlation treatment (truncation of the many-particle

[4] In passing, we note that this orbital-based approach is not the only way for describing the electron cloud, but there are numerous alternatives, for instance by optimizing the electron density (wave function) in real space (see e.g. [5] and references therein.

[5] Of course the other and today more popular way for describing the N-electron expansion is the density-functional theory, see e.g. [6]; a topic that deserves its own lecture course.

[6] Assuming a molecule *in vacuo*, at 0 K

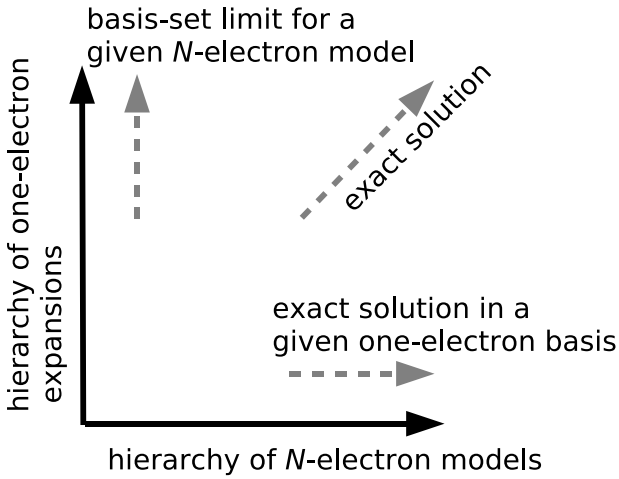


Figure 1.1: The two-way hierarchy of approximate molecular wave functions

space), and the description of the one-particle space, i.e. the basis set used as well as the choice of the molecular Hamiltonian. This is schematically illustrated in Fig. 1.2. A treatment based on the Schrödinger equation (1.1) with an effective electronic Hamiltonian describing non-relativistic (NR) kinematics (1.6), is adequate only for systems containing the lightest elements, located in the first and second row of the Periodic Table. For systems containing heavier elements, a treatment taking into account the effects from special relativity, will be needed. This will be addressed in Chapter 7.

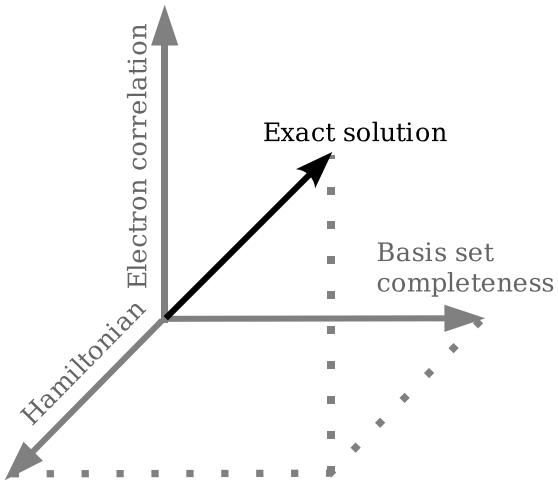


Figure 1.2: The three features determining the accuracy of a quantum chemical calculation.

1.5 Further reading

- R. McWeeny, *Methods for Molecular Quantum Mechanics* (Academic Press 1992)
- R. E. Moss, *Advanced Molecular Quantum Mechanics* (Chapman & Hall 1973)

Chapter 2

Exact and approximate wave functions

2.1 Characteristics of the exact wave function

We shall need to approximate the molecular wave function – perhaps drastically – in order to reach the applicability to molecules with multiple atomic cores and several electrons. The approximations should, however, carried out with care. For this reason, we will now list down the properties (either rationalized earlier or simply taken for granted) that an exact wave function would possess, and on this basis we should seek an approximate solution that retains as many of the following properties as possible.

The exact molecular electronic wave function Ψ

1. is *antisymmetric* with respect to the permutation of any pair of the electrons:

$$\hat{P}\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \epsilon_P \Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) \tag{2.1}$$

   where $\epsilon_P = \pm 1$ for even and odd number of permutations, respectively.

2. is *square-integrable* everywhere in space,

$$\langle \Psi | \Psi \rangle = a \in \mathbb{R} \tag{2.2}$$

3. is *variational* in the sense that for all possible variations $\delta\Psi$, which are orthogonal to the wave function, the energy remains unchanged:

$$\langle \delta\Psi | \Psi \rangle = 0 \Rightarrow \langle \delta\Psi | H | \Psi \rangle = 0 \tag{2.3}$$

4. is *size-extensive*; for a system containing *non-interacting* subsystems the total energy is equal to the sum of the energies of the individual systems.

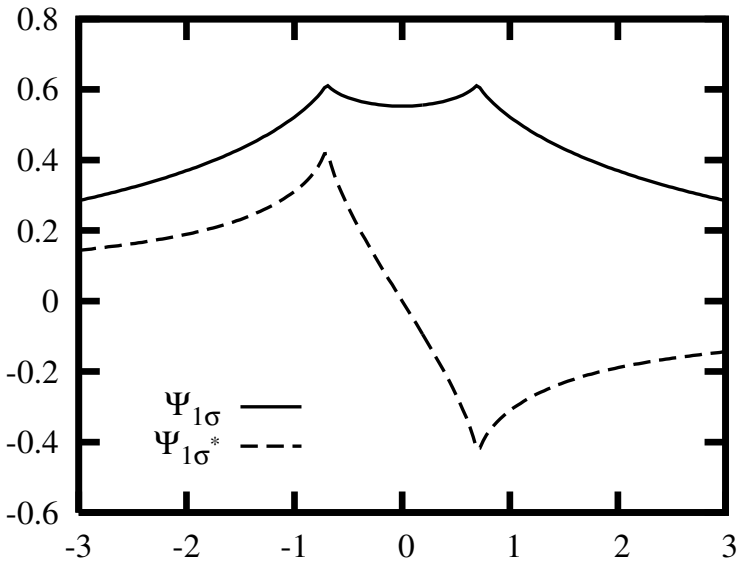


Figure 2.1: Nuclear cusps. Wave functions corresponding to the two lowest eigenvalues of H_2 molecule, along the H–H bond.

5. Within the non-relativistic theory, the exact stationary states are *eigenfunctions of the total and projected spin operators*,

$$\hat{S}^2\Psi = S(S+1)\Psi \tag{2.4}$$
$$\hat{S}_z\Psi = M\Psi \tag{2.5}$$

6. The molecular electronic Hamiltonian (1.6) is singular for $\mathbf{r}_i = \mathbf{r}_j$ and thus the exact wave function must possess a characteristic non-differentiable behavior for spatially coinciding electrons, known as the *electronic Coulomb cusp condition*,

$$\lim_{r_{ij}\to 0}\left(\frac{\partial\Psi}{\partial r_{ij}}\right)_{\text{ave}} = \frac{1}{2}\Psi(r_{ij}=0), \tag{2.6}$$

the description of which is a major obstacle in the accurate practical modelling of the electronic wave function. There exists a condition similar to (2.6) also for electrons coinciding *point-like* nuclei, known as the *nuclear cusp condition*.

7. It may shown that at large distances the *electron density* decays as

$$\rho(r) \sim \exp(-2^{3/2}\sqrt{I}r), \tag{2.7}$$

where I is the ionization potential of the molecule.

8. The exact wave function transforms in a characteristic manner under gauge transformations of the potentials associated with electromagnetic fields, ensuring that all molecular properties described by the wave function are unaffected by the transformations.

As we saw in Chapter 1, some of these – square integrability and Pauli principle – are included straightforwardly, whereas size-extensivity and the cusp condition are more difficult to impose but still desirable. Others are of interest only in special situations.

2.2 Electron correlation

2.2.1 Electron density functions

Ignoring any concerns about the interpretation, let us define the function

$$\rho_1(\mathbf{x}_1) = N \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\Psi^*(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) d\mathbf{x}_2 \cdots d\mathbf{x}_N, \tag{2.8}$$

and an *electron density function* that are observable by e.g. X-ray crystallography, by integrating ρ over spin,

$$P_1(\mathbf{r}_1) = \int \rho(\mathbf{x}_1) d\sigma_1. \tag{2.9}$$

It is possible to introduce corresponding density functions for different configurations of any number of particles; e.g. for two particles as

$$\rho_2(\mathbf{x}_1, \mathbf{x}_2) = N(N-1) \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\Psi^*(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) d\mathbf{x}_3 \cdots d\mathbf{x}_N \tag{2.10}$$

$$P_2(\mathbf{r}_1, \mathbf{r}_2) = \int \pi(\mathbf{x}_1, \mathbf{x}_2) d\sigma_1 d\sigma_2. \tag{2.11}$$

These determine the *two-electron densities* and tell us how the motions of two electrons are *correlated* as a result of their interaction. Because electrons interact only in pairs (i.e. there are no many-body effects), there is no need to consider any higher distribution functions than the pair functions.

2.2.2 Example: Density functions of He

Let us consider the $1s2s$ singlet and triplet states of the helium atom,

$$\begin{aligned}
{}^1\Psi(\mathbf{x}_1, \mathbf{x}_2) &= \frac{1}{2}\left[\chi_{100}(\mathbf{r}_1)\chi_{200}(\mathbf{r}_2) + \chi_{200}(\mathbf{r}_1)\chi_{100}(\mathbf{r}_2)\right]\left[\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)\right] \\
{}^3\Psi(\mathbf{x}_1, \mathbf{x}_2) &= \frac{1}{\sqrt{2}}\left[\chi_{100}(\mathbf{r}_1)\chi_{200}(\mathbf{r}_2) - \chi_{200}(\mathbf{r}_1)\chi_{100}(\mathbf{r}_2)\right] \\
&\quad \times \begin{cases} \alpha(\sigma_1)\alpha(\sigma_2) & M = +1 \\ \frac{1}{\sqrt{2}}\left[\alpha(\sigma_1)\beta(\sigma_2) + \beta(\sigma_1)\alpha(\sigma_2)\right] & M = \ \ 0 \\ \beta(\sigma_1)\beta(\sigma_2) & M = -1 \end{cases}
\end{aligned}$$

For the singlet state, we have

$$\rho(\mathbf{x}_1) = 2 \times \frac{1}{4} \int \left|\chi_{100}(\mathbf{r}_1)\chi_{200}(\mathbf{r}_2) + \chi_{200}(\mathbf{r}_1)\chi_{100}(\mathbf{r}_2)\right|^2 \left|\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)\right|^2 d\mathbf{r}_2 d\sigma_2$$

$$= \frac{1}{2}\left[|\chi_{100}(\mathbf{r}_1)|^2 + |\chi_{200}(\mathbf{r}_1)|^2\right]\left[|\alpha(\sigma_1)|^2 + |\beta(\sigma_1)|^2\right]$$

$$P(\mathbf{r}_1) = \int \rho(\mathbf{x}_1)d\sigma_1 = |\chi_{100}(\mathbf{r}_1)|^2 + |\chi_{200}(\mathbf{r}_1)|^2 .$$

ρ can be rewritten as

$$\rho(\mathbf{x}_1) = P_\alpha(\mathbf{r}_1)\,|\alpha(\sigma_1)|^2 + P_\beta(\mathbf{r}_1)\,|\beta(\sigma_1)|^2 ,$$

where the first term vanishes unless $\sigma_1 = +1/2$ and the second unless $\sigma_1 = -1/2$, and thus

$$P_\alpha(\mathbf{r}_1) = \frac{1}{2}P(\mathbf{r}_1) \text{ density for spin-up electrons}$$
$$P_\beta(\mathbf{r}_1) = \frac{1}{2}P(\mathbf{r}_1) \text{ density for spin-down electrons}$$

These densities are always equal in a singlet state, but in non-singlet states the α and β-densities differ, giving a resultant *spin density*. For the first triplet state we obtain

$$P_\alpha(\mathbf{r}_1) = 1, \;\; P_\beta(\mathbf{r}_1) = 0$$

and for the third

$$P_\alpha(\mathbf{r}_1) = 0, \;\; P_\beta(\mathbf{r}_1) = 1,$$

while for the second we get

$$P_\alpha(\mathbf{r}_1) = P_\beta(\mathbf{r}_1) = \frac{1}{2}P(\mathbf{r}_1).$$

2.2.3 Generalized density functions

Consider a 1-electron system, an electron described by a spin-orbital ψ. The expectation value in this state of any quantity described by operator $\hat{F}$ is given by $\langle\hat{F}\rangle = \int \psi^*(\mathbf{x})\hat{F}\psi(\mathbf{x})d\mathbf{x}$. We can rewrite this as

$$\langle\hat{F}\rangle = \int_{\mathbf{x}'=\mathbf{x}} \hat{F}\psi(\mathbf{x})\psi^*(\mathbf{x}')d\mathbf{x} = \int_{\mathbf{x}'=\mathbf{x}} \hat{F}\rho(\mathbf{x};\mathbf{x}')d\mathbf{x}$$

by having agreed that $\hat{F}$ works on functions of $\mathbf{x}$ only and setting $\mathbf{x}' = \mathbf{x}$ after operating with $\hat{F}$ but before completing the integration. We define the *generalized density functions* as

$$\rho(\mathbf{x}_1;\mathbf{x}_1') = N\int \Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)\Psi^*(\mathbf{x}_1',\mathbf{x}_2,\ldots,\mathbf{x}_N)d\mathbf{x}_2\cdots d\mathbf{x}_N \tag{2.12}$$

$$\pi(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') = N(N-1)\int \Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)\Psi^*(\mathbf{x}_1',\mathbf{x}_2',\ldots,\mathbf{x}_N)d\mathbf{x}_3\cdots d\mathbf{x}_N \tag{2.13}$$

We may discuss *all* one-electron properties in terms of $\rho(\mathbf{x}_1;\mathbf{x}'_1)$ and *all* two-electron properties in terms of $\pi(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2)$. The spinless analogues are given by

$$P(\mathbf{r}_1;\mathbf{r}'_1) = \int_{\sigma'_1=\sigma_1} \rho(\mathbf{x}_1;\mathbf{x}'_1)d\sigma_1 \tag{2.14}$$

$$\Pi(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}'_1,\mathbf{r}'_2) = \int_{\sigma'_1=\sigma_1}\int_{\sigma'_2=\sigma_2} \pi(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2)d\sigma_1 d\sigma_2. \tag{2.15}$$

2.2.4 The pair function

Let us write the spin-dependence explicitly also in the case of π:

$$\begin{aligned}\pi(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2) = {} & \Pi_{\alpha\alpha,\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}'_1,\mathbf{r}'_2)\alpha(\sigma_1)\alpha(\sigma_2)\alpha^*(\sigma'_1)\alpha^*(\sigma'_2) \\ & +\Pi_{\alpha\beta,\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}'_1,\mathbf{r}'_2)\alpha(\sigma_1)\beta(\sigma_2)\alpha^*(\sigma'_1)\beta^*(\sigma'_2)+\ldots\end{aligned} \tag{2.16}$$

which reduces to a four-component quantity when spin is integrated over. Eq. (2.16) can be written in our notation for the diagonal components, $\Pi_{\alpha\alpha,\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}_1,\mathbf{r}_2) = \Pi_{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2)$ etc., as

$$\Pi(\mathbf{r}_1,\mathbf{r}_2) = \Pi_{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2)+\Pi_{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2)+\Pi_{\beta\alpha}(\mathbf{r}_1,\mathbf{r}_2)+\Pi_{\beta\beta}(\mathbf{r}_1,\mathbf{r}_2), \tag{2.17}$$

where each component resembles a contribution to the pair function Π from electrons at $\mathbf{r}_1$ and $\mathbf{r}_2$ with spins indicated by the subscript as well as the probability of each spin-configuration. The two other six non-zero terms in (2.16) vanish in the spin-integration.

The pair-function components in the simple case of a system described by one determinant of spin-orbitals [c.f. Eqs. (2.37) and (2.36)] are (with the similar terms obtained by $\alpha \leftrightarrow \beta$)

$$\Pi_{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2) = P_\alpha(\mathbf{r}_1)P_\alpha(\mathbf{r}_2) - P_\alpha(\mathbf{r}_2;\mathbf{r}_1)P_\alpha(\mathbf{r}_1;\mathbf{r}_2), \tag{2.18}$$

$$\Pi_{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2) = P_\alpha(\mathbf{r}_1)P_\beta(\mathbf{r}_2). \tag{2.19}$$

From these results we can begin to construct a picture on electron correlation, keeping the one-determinant approximation in mind: From the latter equation we see that there is no correlation between the positions of electrons of opposite spins, whilst electrons of like spin are correlated as their pair function vanishes for $\mathbf{r}_2 \to \mathbf{r}_1$. This special type of correlation, referred to as *Fermi correlation*, prevents electrons of like spin to coincidence in space.

If we leave the one-determinant approximation and suppose that Ψ is an exact many-electron wave function, the following ramifications for electron correlation hold.

1. $\Pi_{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2)$ and $\Pi_{\beta\beta}(\mathbf{r}_1,\mathbf{r}_2)$ both vanish like r_{12}^2 for $\mathbf{r}_2 \to \mathbf{r}_1$, giving zero probability of finding two electrons of like spin at the same point in space. This follows from the antisymmetry of Ψ and the resulting antisymmetry of $\Pi_{\alpha\alpha,\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}'_1,\mathbf{r}'_2)$ and $\Pi_{\alpha\alpha,\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}'_1,\mathbf{r}'_2)$ in both pairs of variables; and may be regarded as the most general statement of the Pauli exclusion principle.

2. By writing $\Pi_{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) = P_\alpha(\mathbf{r}_1)P_\alpha(\mathbf{r}_2)[1 + f^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2)]$ we may define the *correlation hole* or the Coulomb hole

$$\frac{\Pi_{\alpha\alpha}}{P_\alpha(\mathbf{r}_2)} - P_\alpha(\mathbf{r}_1) = P_\alpha(\mathbf{r}_1) f^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2),$$

i.e., the difference between the probability of finding a spin-up electron in $\mathbf{r}_1$ when one spin-up electron is at $\mathbf{r}_2$ and the same probability in the absence of the second electron. The form of the correlation factor f is known for dilute electron gas, but unknown in the case of complicated potential present in a molecular system. Clearly, the Fermi correlation requires that $f^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) \to -1$ for $\mathbf{r}_2 \to \mathbf{r}_1$. This "hole" integrates to -1:

$$\int P_\alpha(\mathbf{r}_1) f^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 = -1 \; \forall \, \mathbf{r}_2.$$

3. Similarly, if we write

$$\Pi_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) = P_\alpha(\mathbf{r}_1)P_\beta(\mathbf{r}_2)[1 + f^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2)]$$

then the correlation hole integrates to zero:

$$\int P_\alpha(\mathbf{r}_1) f^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 = 0 \; \forall \, \mathbf{r}_2.$$

The probability should be decreased (i.e. $f < 0$) near the reference electron due to the Coulomb repulsion but enhanced further away.

4. The hole function is also known to have a discontinuity of slope, or "cusp" for $\mathbf{r}_1 \to \mathbf{r}_2$. See Section 2.2.5 for further discussion.

2.2.5 Example: Coulomb and nuclear cusps in He

The non-relativistic Hamiltonian of the helium-like atom with the origin at the nucleus,

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{|\mathbf{r}_1|} - \frac{Z}{|\mathbf{r}_2|} + \frac{1}{|\mathbf{r}_i - \mathbf{r}_2|}$$

has singularities for $\mathbf{r}_1 = \mathbf{0}$, $\mathbf{r}_2 = \mathbf{0}$, and for $\mathbf{r}_1 = \mathbf{r}_2$. At these points, the exact solution to the Schrödinger equation must provide contributions that balance the singularities such that the *local energy*

$$\epsilon(\mathbf{r}_1, \mathbf{r}_2) = \frac{\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2)}{\Psi(\mathbf{r}_1, \mathbf{r}_2)} \tag{2.20}$$

remains constant and equal to the eigenvalue E. The only possible "source" for this balancing is the kinetic energy. It is convenient to employ the symmetry of the helium

atom and express the kinetic energy operator in terms of three radial coordinates r_1, r_2 and r_{12}, such that the Hamiltonian is written as

$$\begin{aligned}\hat{H} = & -\frac{1}{2}\sum_{i=1}^{2}\left(\frac{\partial^2}{\partial r_i^2}+\frac{2}{r_i}\frac{\partial}{\partial r_i}+\frac{2Z}{r_i}\right)-\left(\frac{\partial^2}{\partial r_{12}^2}+\frac{2}{r_{12}}\frac{\partial}{\partial r_{12}}-\frac{1}{r_{12}}\right) \\ & -\left(\frac{\mathbf{r}_1}{r_1}\cdot\frac{\mathbf{r}_{12}}{r_{12}}\frac{\partial}{\partial r_1}+\frac{\mathbf{r}_2}{r_2}\cdot\frac{\mathbf{r}_{21}}{r_{21}}\frac{\partial}{\partial r_2}\right)\frac{\partial}{\partial r_{12}}. \end{aligned} \tag{2.21}$$

The terms that multiply $1/r_{12}$ at $r_{12}=0$ must vanish in $\hat{H}\Psi$, which imposes a condition

$$\left.\frac{\partial\Psi}{\partial r_{12}}\right|_{r_{12}=0} = \frac{1}{2}\Psi(r_{12}=0) \tag{2.22}$$

on the wave function. Similarly, the singularities at the nucleus are now seen to be balanced by the kinetic energy terms proportional to $1/r_i$:

$$\left.\frac{\partial\Psi}{\partial r_i}\right|_{r_i=0} = -Z\Psi(r_i=0). \tag{2.23}$$

Eq. (2.22) describes the situation when the electrons coincide in space and is referred to as the *Coulomb cusp condition*; whereas Eq. (2.23) establishes the behavior of the ground-state wave function in the vicinity of the nucleus and is known as the *nuclear cusp condition*.

Expanding the ground-state helium wave function around $r_2=r_1$ and $r_{12}=0$ we obtain

$$\Psi(r_1,r_2,0) = \Psi(r_1,r_1,0)+(r_2-r_1)\left.\frac{\partial\Psi}{\partial r_2}\right|_{r_2=r_1}+r_{12}\left.\frac{\partial\Psi}{\partial r_{12}}\right|_{r_2=r_1}+\ldots,$$

which gives, when the cusp condition (2.22) is applied

$$\Psi(r_1,r_2,0) = \Psi(r_1,r_1,0)+(r_2-r_1)\left.\frac{\partial\Psi}{\partial r_2}\right|_{r_2=r_1}+\frac{1}{2}|\mathbf{r}_2-\mathbf{r}_1|\Psi(r_1,r_1,0)+\ldots$$

Therefore, the cusp condition leads to a wave function that is continuous but not smooth (discontinuous first derivative) at r_{12}.

The nuclear cusp condition for the "first" electron when the wave function does not vanish at $r_1=0$ (such as the helium ground state) is satisfied if the wave function exhibits an exponential dependence on r_1 close to the nucleus:

$$\Psi(r_1,r_2,r_{12}) = \exp(-Zr_1)\Psi(0,r_2,r_{12}) \approx (1-Zr_1)\Psi(0,r_2,r_{12}).$$

Molecular electronic wave functions are usually expanded in simple analytical functions centered on the atomic nuclei (AOs), and close to a given nucleus, the behavior of the wave function is dominated by the analytical form of the AOs. In particular, the Slater-type orbitals, introduced in Section 6.1.4, are compatible with the nuclear cusp condition, while the Gaussian-type orbitals are not.

It should be noted that the cusp conditions in Eqs. (2.22) and (2.23) are written for the totally symmetric singlet ground state of the helium atom. The cusp conditions in a more general situation (but still for a wave function that does not vanish at the singularities) should be written as

$$\lim_{r_{ij}\to 0}\left(\frac{\partial\Psi}{\partial r_{ij}}\right)_{\text{ave}} = \frac{1}{2}\Psi(r_{ij}=0) \tag{2.24}$$

$$\lim_{r_i\to 0}\left(\frac{\partial\Psi}{\partial r_i}\right)_{\text{ave}} = -Z\Psi(r_i=0), \tag{2.25}$$

where the averaging over all directions is implied.

2.2.6 Electron correlation summary

Let us at this stage review some nomenclature of electron correlation used in molecular electronic-structure theory.

- A commonly-used concept, *correlation energy* [7], has a pragmatic definition

  $$E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}},$$

  where, in a given one-electron basis, E_{HF} is a best one-determinant total energy and E_{exact} the "exact" energy featuring all possible Slater determinants of the system in the given one-electron basis. This definition is most usable when speaking of molecular ground states and equilibrium geometries, while outside them it is untenable.

- *Fermi correlation* arises from the Pauli antisymmetry of the wave function and is taken into account already at the single-determinant level.

- *Static correlation*, also known as near-degeneracy or nondynamical correlation, arises from the near-degeneracy of electronic configurations.

- *Dynamical correlation* is associated with the instantaneous correlation among the electrons arising from their mutual Coulombic repulsion. It is useful to distinguish between

  - *long-range dynamical correlation* and
  - *short-range dynamical correlation*, which is related to the singularities in the Hamiltonian and correspondingly to the Coulomb cusp in the wave function.

2.3 Electron density

2.3.1 Electronic energy by density

The individual expectation values for terms in the electronic Hamiltonian obtain the following expressions using the general density functions:

$$\left\langle \sum_i \hat{h}_i \right\rangle = \int_{\mathbf{x}'_1=\mathbf{x}_1} \hat{h}_1 \, \rho(\mathbf{x}_1;\mathbf{x}'_1) d\mathbf{x}_1 \tag{2.26}$$

$$\left\langle \sum_i \hat{V}_i \right\rangle = \int_{\mathbf{x}'_1=\mathbf{x}_1} \hat{V}_1 \, \rho(\mathbf{x}_1;\mathbf{x}'_1) d\mathbf{x}_1 = \int \hat{V}_1 \rho(\mathbf{x}_1) d\mathbf{x}_1 \tag{2.27}$$

$$\left\langle {\sum_{ij}}' \hat{g}_{ij} \right\rangle = \int_{\mathbf{x}'_1=\mathbf{x}_1} \int_{\mathbf{x}'_2=\mathbf{x}_2} \hat{g}_{12} \, \pi(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2) d\mathbf{x}_1 d\mathbf{x}_2 = \int \hat{g}_{12} \, \pi(\mathbf{x}_1,\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \tag{2.28}$$

The latter expressions for $\langle \sum_i \hat{V}_i \rangle$ and $\langle {\sum_{ij}}' \hat{g}_{ij} \rangle$ are obtained by noting that $\hat{V}_1 = V(\mathbf{r}_1)$ is just a factor in the integrand, as is $\hat{g}_{12}$, and thus the primes may be omitted. Therefore, the general expression for the N-electron system with the usual molecular Hamiltonian Eq. (1.6) takes a simple form

$$E = -\frac{1}{2} \int \nabla^2 \rho(\mathbf{x}_1) d\mathbf{x}_1 + \sum_{I=1}^{K} \int |\mathbf{r}_1 - \mathbf{R}_I|^{-1} \, \rho(\mathbf{x}_1) d\mathbf{x}_1 + \frac{1}{2} \int |\mathbf{r}_1 - \mathbf{r}_2|^{-1} \, \pi(\mathbf{x}_1,\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2, \tag{2.29}$$

or, by carrying out the spin-integration,

$$\begin{aligned} E &= -\frac{1}{2} \int \nabla^2 P(\mathbf{r}_1) d\mathbf{r}_1 + \sum_{I=1}^{K} \int |\mathbf{r}_1 - \mathbf{R}_I|^{-1} \, P(\mathbf{r}_1) d\mathbf{r}_1 + \frac{1}{2} \int |\mathbf{r}_1 - \mathbf{r}_2|^{-1} \, \Pi(\mathbf{r}_1,\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= T + V_{en} + V_{ee}. \end{aligned} \tag{2.30}$$

It should be emphasized that these results are valid for all kinds of states and their approximate wave functions of any system. Furthermore, for evaluation of molecular energies and properties, we do not even need to construct the N-electron wave function, but everything is exactly described by the electron densities.

2.3.2 Fock–Dirac density matrix

Let us carry out the same for a single Slater determinant Ψ, that we recall to provide an useful approximation for the ground state wave function, by considering N spin-orbitals having the orbital factor corresponding to an occupied MO. The energy expression is given by

$$E = \left\langle \Psi \left| \hat{H} \right| \Psi \right\rangle = \sum_{r \in \text{occ}} \left\langle \psi_r \left| \hat{h} \right| \psi_r \right\rangle + \frac{1}{2} \sum_{rs \in \text{occ}} \left(\langle \psi_r \psi_s \left| \hat{g} \right| \psi_r \psi_s \rangle - \langle \psi_r \psi_s \left| \hat{g} \right| \psi_s \psi_r \rangle \right) \tag{2.31}$$

Assume that we may expand $\rho(\mathbf{x}_1, \mathbf{x}_1')$ in spin-orbitals as

$$\rho(\mathbf{x}_1, \mathbf{x}_1') = \sum_{rs} \rho_{rs} \psi_r(\mathbf{x}_1) \psi_s^*(\mathbf{x}_1'), \tag{2.32}$$

where the ρ_{rs} are numerical coefficients; then the expectation value (2.26) can be written as the trace of a matrix product:

$$\left\langle \sum_i \hat{h}_i \right\rangle = \sum_{rs} \rho_{rs} \left\langle \psi_s \left| \hat{h} \right| \psi_r \right\rangle = \mathrm{Tr}[\boldsymbol{\rho}\mathbf{h}], \tag{2.33}$$

and by comparing to the general expression, we observe that in the one-determinant approximation $\rho_{RS} = \delta_{RS}$. The one-determinant approximation to $\rho(\mathbf{x}_1; \mathbf{x}_1')$ may now be written as

$$\rho(\mathbf{x}_1; \mathbf{x}_1') = \sum_{r \in \mathrm{occ}} \psi_r(\mathbf{x}_1) \psi_r^*(\mathbf{x}_1'). \tag{2.34}$$

The expression for π follows in a similar manner, and we find

$$\begin{aligned} \pi(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2') &= \sum_{rs} [\psi_r(\mathbf{x}_1)\psi_s(\mathbf{x}_2)\psi_r^*(\mathbf{x}_1')\psi_s^*(\mathbf{x}_2') - \psi_r(\mathbf{x}_2)\psi_s(\mathbf{x}_1)\psi_r^*(\mathbf{x}_2')\psi_s^*(\mathbf{x}_1')] & (2.35) \\ &= \rho(\mathbf{x}_1; \mathbf{x}_1')\rho(\mathbf{x}_2; \mathbf{x}_2') - \rho(\mathbf{x}_2; \mathbf{x}_1')\rho(\mathbf{x}_1; \mathbf{x}_2'). & (2.36) \end{aligned}$$

The factorization of the two-electron density matrix in terms of the one-electron ρ is characteristic to the one-determinant approximation: it means that in this approximation everything is determined by the function ρ (often called as the *Fock–Dirac density matrix*).

So far, we have included spin implicitly through the use of spin-orbitals. In the one-determinant case the we may write spin explicitly, for the case $\mathbf{x}_1' = \mathbf{x}_1$,

$$\rho(\mathbf{x}_1) = P_\alpha(\mathbf{r}_1)\alpha(\sigma_1)\alpha^*(\sigma_1) + P_\beta(\mathbf{r}_1)\beta(\sigma_1)\beta^*(\sigma_1), \tag{2.37}$$

where the densities for spin-up and spin-down electrons are

$$P_\alpha(\mathbf{r}_1) = \sum_{s(\alpha)} \phi_s(\mathbf{r}_1)\phi_s^*(\mathbf{r}_1), \qquad P_\beta(\mathbf{r}_1) = \sum_{s(\beta)} \phi_s(\mathbf{r}_1)\phi_s^*(\mathbf{r}_1). \tag{2.38}$$

By integrating ρ over spin, we obtain the electron density in the form

$$P(\mathbf{r}_1) = P_\alpha(\mathbf{r}_1) + P_\beta(\mathbf{r}_1) \tag{2.39}$$

that is, a sum of spin-up and spin-down densities. The excess of spin-up density over spin-down density,

$$Q_z(\mathbf{r}_1) = \frac{1}{2} \left[P_\alpha(\mathbf{r}_1) - P_\beta(\mathbf{r}_1) \right], \tag{2.40}$$

is an useful quantity, which is in fact the density of spin angular momentum around the z-axis. $P(\mathbf{r})$ and $Q_z(\mathbf{r})$ are enough to determine all the properties of the electron distribution in the one-determinant approximation.

2.3.3 Example: Closed-shell energy

Let us finally consider an important special case, a closed-shell system, in which all spin-orbitals are doubly occupied, once with α and once with β electron; meaning that $P_\alpha = P_\beta = P/2$ and the spin density is everywhere zero. In this case,

$$P(\mathbf{r}_1) = 2 \sum_{s \in \mathrm{occ}} \phi_s(\mathbf{r}_1)\phi_s^*(\mathbf{r}_1), \tag{2.41}$$

and by substituting Eq. (2.37) to Eq. (2.36) we find

$$\Pi(\mathbf{r}_1, \mathbf{r}_2) = P(\mathbf{r}_1)P(\mathbf{r}_2) - \frac{1}{2}P(\mathbf{r}_2; \mathbf{r}_1)P(\mathbf{r}_1; \mathbf{r}_2). \tag{2.42}$$

Substituting these expressions to Eq. (2.30) we obtain an often-used expression for the closed-shell energy:

$$E = 2\sum_r \left\langle \phi_r \left| \hat{h} \right| \phi_r \right\rangle + \sum_{rs} \left[2 \left\langle \phi_r\phi_s \left| \hat{g} \right| \phi_r\phi_s \right\rangle - \left\langle \phi_r\phi_s \left| \hat{g} \right| \phi_s\phi_r \right\rangle \right]. \tag{2.43}$$

2.3.4 Other density functions

Other property densities, in addition to the charge density $P(\mathbf{r})$ and the spin-density $Q_z(\mathbf{r})$, could be defined in the same way. For example, referring to Eq. (2.30),

$$T(\mathbf{r}) = \left[\frac{\hat{p}^2}{2} P(\mathbf{r}; \mathbf{r}') \right]_{\mathbf{r}'=\mathbf{r}} \qquad (\hat{p}^2 = \hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2)$$

would be a kinetic-energy density, since $T(\mathbf{r})d\mathbf{r}$ is the contribution to $\langle T \rangle$ associated with volume element $d\mathbf{r}$ at $\mathbf{r}$. However, point contributions to real observables are not necessarily real, and the proper definition of the *kinetic-energy density* is

$$T(\mathbf{r}) = \left[\frac{\hat{\mathbf{p}} \cdot \hat{\mathbf{p}}^\dagger}{2} P(\mathbf{r}; \mathbf{r}') \right]_{\mathbf{r}'=\mathbf{r}}. \tag{2.44}$$

where the adjoint operator is understood to work on the primed variable only.

Another often encountered density function is the *current density*

$$J_\mu(\mathbf{r}) = \frac{1}{2} \left[(\hat{p}_\mu + \hat{p}_\mu^\dagger) P(\mathbf{r}; \mathbf{r}') \right]_{\mathbf{r}'=\mathbf{r}} = \mathrm{Re} \left[\hat{p}_\mu P(\mathbf{r}; \mathbf{r}') \right]_{\mathbf{r}'=\mathbf{r}}, \tag{2.45}$$

where μ denotes the Cartesian x, y, z components. For a system in a stationary state described by a real wave function $\mathbf{J} = \mathbf{0}$, but for a system in the presence of a magnetic field, circulating currents are always present. A more general form of $\mathbf{J}$ is obtained on introducing field terms in the Hamiltonian via the gauge-invariant momentum operator,

$$\hat{\mathbf{p}} \to \hat{\boldsymbol{\pi}} = \hat{\mathbf{p}} + \mathbf{A}, \tag{2.46}$$

where $\mathbf{A}$ is the magnetic vector potential from the applied field is derived. The corresponding current density is

$$J_\mu(\mathbf{r}) = \mathrm{Re}\left[\hat{\pi}_\mu P(\mathbf{r})\right]. \tag{2.47}$$

The kinetic energy density is also modified by the presence of the field, and (2.44) becomes

$$T(\mathbf{r}) = \left[\frac{\hat{\boldsymbol{\pi}} \cdot \hat{\boldsymbol{\pi}}^\dagger}{2} P(\mathbf{r};\mathbf{r}')\right]_{\mathbf{r}'=\mathbf{r}}.$$

Finally; it may be shown that for a wave function that satisfies the time-dependent Schrödinger equation the charge density and the current density satisfy the conservation equation

$$\nabla \cdot \mathbf{J}(\mathbf{r}) = -\frac{\partial P(\mathbf{r})}{\partial t}. \tag{2.48}$$

When Ψ is an exact stationary-state function, P is time-independent and the net flux of density out of any region is zero; but with $\mathbf{A} \neq \mathbf{0}$ there will be in general a steady-state distribution of non-zero *currents*, satisfying the usual continuity equation $\nabla \cdot \mathbf{J} = 0$.

2.4 On the optimization of the wave function

2.4.1 Variation method

According to the *variation principle*, the solution of the time-independent Schrödinger equation $\hat{H}\left|\Psi\right\rangle = E\left|\Psi\right\rangle$ is equivalent to an optimization of the energy functional

$$E[\tilde{\Psi}] = \frac{\left\langle \tilde{\Psi} \middle| \hat{H} \middle| \tilde{\Psi} \right\rangle}{\left\langle \tilde{\Psi} \middle| \tilde{\Psi} \right\rangle}, \tag{2.49}$$

where $\left|\tilde{\Psi}\right\rangle$ is some approximation to the eigenstate $\left|\Psi\right\rangle$. It provides a simple and powerful procedure for generating approximate wave functions: for some proposed model for the wave function, we express the electronic state $\left|\mathbf{C}\right\rangle$ in terms of a finite set of numerical parameters; the stationary points of energy function

$$E(\mathbf{C}) = \frac{\left\langle \mathbf{C} \middle| \hat{H} \middle| \mathbf{C} \right\rangle}{\left\langle \mathbf{C} \middle| \mathbf{C} \right\rangle} \tag{2.50}$$

are the approximate electronic states $\left|\mathbf{C}\right\rangle$ and the values $E(\mathbf{C})$ at the stationary points the approximate energies. Due to the variation principle, the expectation value of the Hamiltonian is correct to second order in the error.

2.4.2 Electronic gradient and Hessian

A simple realization of the variation method is to make a linear ansatz for the wave function,

$$|\mathbf{C}\rangle = \sum_{i=1}^{m} C_i \, |i\rangle \, ,$$

i.e. the approximate state is expanded as a linear combination of m Slater determinants. We further assume here that the wave function is real. The energy function of this state is given by Eq. (2.50). In order to locate and to characterize the stationary points, we shall employ the first and second derivatives with respect to the variational parameters:

$$\begin{aligned} E_i^{(1)}(\mathbf{C}) &= \frac{\partial E(\mathbf{C})}{\partial C_i} = 2\frac{\left\langle i \left| \hat{H} \right| \mathbf{C} \right\rangle - E(\mathbf{C}) \, \langle i \, | \mathbf{C} \rangle}{\langle \mathbf{C} \, | \mathbf{C} \rangle} \\ E_{ij}^{(2)}(\mathbf{C}) &= \frac{\partial^2 E(\mathbf{C})}{\partial C_i \partial C_j} = 2\frac{\left\langle i \left| \hat{H} \right| j \right\rangle - E(\mathbf{C}) \, \langle i \, | j \rangle}{\langle \mathbf{C} \, | \mathbf{C} \rangle} - 2E_i^{(1)}(\mathbf{C})\frac{\langle j \, | \mathbf{C} \rangle}{\langle \mathbf{C} \, | \mathbf{C} \rangle} - 2E_j^{(1)}(\mathbf{C})\frac{\langle i \, | \mathbf{C} \rangle}{\langle \mathbf{C} \, | \mathbf{C} \rangle}, \end{aligned}$$

known as the *electronic gradient* and *electronic Hessian*, respectively.

The condition for stationary points, $\left\langle i \left| \hat{H} \right| \mathbf{C} \right\rangle = E(\mathbf{C}) \, \langle i \, | \mathbf{C} \rangle$ is in a matrix form equal to $\mathbf{HC} = E(\mathbf{C})\mathbf{SC}$, where the Hamiltonian and overlap matrix are given by $H_{ij} = \left\langle i \left| \hat{H} \right| j \right\rangle$ and $S_{ij} = \langle i \, | j \rangle$. Assuming that $\mathbf{S} = \mathbf{1}$, we have to solve a standard m-dimensional eigenvalue problem with m orthonormal solutions $C_K = (C_{1K} \, C_{2K} \, \cdots C_{mK})^T$, $\mathbf{C}_K^T \mathbf{C}_K = \delta_{KL}$, with the associated real eigenvalues $E_K = E(\mathbf{C}_K)$, $E_1 \leq E_2 \leq \cdots \leq E_m$.

The eigenvectors represent the approximate wave functions $|K\rangle = \sum_{i=1}^{M} C_{iK} \, |i\rangle$ with a corresponding approximate energy E_K. To characterize the stationary points, we note that the Hessian is at these points ${}^K E_{ij}^{(2)}(\mathbf{C}_K) = 2(\left\langle i \left| \hat{H} \right| j \right\rangle - E_k \, \langle i \, | j \rangle)$. We may also express the Hessian in the basis formed of the eigenvectors:

$${}^K E_{MN}^{(2)} = 2(\left\langle M \left| \hat{H} \right| N \right\rangle - E_K \, \langle M \, | N \rangle) = 2(E_M - E_N)\delta_{MN} \Rightarrow {}^K E_{MM}^{(2)} = 2(E_M - E_K).$$

${}^K E_{MM}^{(2)}$ is thus singular and K^{th} state has exactly $K - 1$ negative eigenvalues. Therefore, in the space orthogonal to $\mathbf{C}_K$, the first solution is a minimum, the second a first-order saddle point, the third a second-order saddle point, and so forth.

2.4.3 Hellmann–Feynman theorem

Many of the theorems for exact wave functions hold also for the approximate ones that are variationally determined. One of the most important is the *Hellmann–Feynman theorem*, which states that the first-order change in the energy due to a perturbation may be calculated as the expectation value of the perturbation operator $\hat{V}$: Let $|\Psi_\alpha\rangle$ be the wave

function associated with $\hat{H} + \alpha\hat{V}$ and $|\Psi\rangle$ unperturbed wave function at $\alpha = 0$. Then

$$\left.\frac{dE(\alpha)}{d\alpha}\right|_{\alpha=0} = \left.\frac{\partial}{\partial\alpha}\frac{\left\langle \Psi_\alpha \left| \hat{H} + \alpha\hat{V} \right| \Psi_\alpha \right\rangle}{\langle \Psi_\alpha | \Psi_\alpha \rangle}\right|_{\alpha=0} = 2\,\mathrm{Re}\left\langle \left.\frac{\partial\Psi_\alpha}{\partial\alpha}\right|_{\alpha=0} \left| \hat{H} - E(0) \right| \Psi \right\rangle + \left\langle \Psi \left| \hat{V} \right| \Psi \right\rangle$$
$$= \left\langle \Psi \left| \hat{V} \right| \Psi \right\rangle. \tag{2.51}$$

In fact, for the Hellmann–Feynman theorem to hold, we need to demand from the approximate wave functions that they are optimized with respect to the changes induced by the perturbation: $|\Psi\rangle \to |\Psi\rangle + \alpha\,|\partial\Psi/\partial\alpha\rangle$. Usually in molecular calculations we construct our wave function from a finite set of analytical functions attached to the atomic nuclei. For example, when we distort the molecular geometry, we change the basis set in terms of which our electronic wave function is expanded, and a wave function optimized at one particular geometry is not accurately represented in terms of a basis set associated with another geometry. As a result, the unperturbed electronic is not variational with respect to these changes and the conditions of the Hellmann–Feynman theorem is not satisfied.

However, this is an artificial difficulty arising from the coordinate representation of quantum mechanics we presently operate in. The picture presented by the second quantization, the necessary conditions are fulfilled and we are able to employ the theorem for approximate wave functions in finite bases in exactly the same manner as for exact wave functions.

2.4.4 The molecular electronic virial theorem

The exact molecular energy is variational with respect to an arbitrary change in the wave function, particularly of interest are the uniform, normalization-preserving scaling of the electron coordinates

$$\Psi(\mathbf{r}_i) \to \Psi_\alpha(\mathbf{r}_i) = \alpha^{3N/2}\Psi(\alpha\mathbf{r}_i).$$

Let us partition the electronic Hamiltonian in a bit different manner than earlier:

$$\hat{H}(\mathbf{R}) = T + V(\mathbf{R}) \tag{2.52}$$
$$\hat{T} = -\frac{1}{2}\sum_i \nabla_i^2 \tag{2.53}$$
$$\hat{V}(\mathbf{R}) = \sum_{i>j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{iI}\frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{I>J}\frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}, \tag{2.54}$$

and applying this decomposition we may find the stationary points of the energy function are found at[1]

$$0 = \frac{\partial}{\partial\alpha}\left\langle \Psi_\alpha \left| \hat{H}(\mathbf{R}) \right| \Psi_\alpha \right\rangle\Big|_{\alpha=1} = \frac{\partial}{\partial\alpha}\left[\alpha^2\left\langle \Psi \left| \hat{T} \right| \Psi \right\rangle + \alpha\left\langle \Psi \left| \hat{V}(\alpha\mathbf{R}) \right| \Psi \right\rangle\right]\Big|_{\alpha=1}$$
$$\Rightarrow\; 2\left\langle \Psi \left| \hat{T} \right| \Psi \right\rangle + \left\langle \Psi \left| \hat{V}(\mathbf{R}) \right| \Psi \right\rangle = -\left\langle \Psi \left| \left.\frac{dV(\alpha\mathbf{R})}{d\alpha}\right|_{\alpha=1} \right| \Psi \right\rangle \overset{\text{H–F}}{=} -\left.\frac{dE(\alpha\mathbf{R})}{d\alpha}\right|_{\alpha=1} \tag{2.55}$$

[1]Note that the unperturbed wave function corresponds here to $\alpha = 1$ instead of $\alpha = 0$.

This result (2.55) is the quantum-mechanical *virial theorem* for a field-free non-relativistic molecular Hamiltonian. The most important observation is that in the molecular equilibrium geometries ($\mathbf{R} = \mathbf{R}_e$), and in the case of atoms

$$\left\langle \Psi \left| \hat{T} \right| \Psi \right\rangle = -\frac{1}{2} \left\langle \Psi \left| \hat{V}(\mathbf{R}_e) \right| \Psi \right\rangle . \tag{2.56}$$

Furthermore,

$$\left\langle \Psi \left| \hat{T} \right| \Psi \right\rangle |_{\mathbf{R}=\mathbf{R}_e} = -E(\mathbf{R}_e), \qquad \left\langle \Psi \left| \hat{V}(\mathbf{R}_e) \right| \Psi \right\rangle = 2E(\mathbf{R}_e). \tag{2.57}$$

Also these expressions hold for any approximate wave function that is variational with respect to a uniform scaling of the nuclear as well as electronic coordinates. Note that according to the last result, no stationary points of positive energy may exist.

The scaling force may be easily related to classical Cartesian forces on the nuclei, $\mathbf{F}_I(\mathbf{R}) = -dE(\mathbf{R})/d\mathbf{R}_I$, by invoking the chain rule

$$\left. \frac{dE(\alpha\mathbf{R})}{d\alpha} \right|_{\alpha=1} = \sum_I \left. \frac{d(\alpha\mathbf{R}_I)}{d\alpha} \right|_{\alpha=1} \left. \frac{dE(\alpha\mathbf{R}_I)}{d(\alpha\mathbf{R}_I} \right|_{\alpha=1} = -\sum_I \mathbf{R}_I \cdot \mathbf{F}_I(\mathbf{R})$$

and combining this with virial theorem, we may extract the Cartesian forces experienced by the nuclei,

$$\sum_I \mathbf{R}_I \cdot \mathbf{F}_I(\mathbf{R}) = 2 \left\langle \Psi \left| \hat{T} \right| \Psi \right\rangle + \left\langle \Psi \left| \hat{V}(\mathbf{R}) \right| \Psi \right\rangle . \tag{2.58}$$

2.5 Further reading

- D. P. Tew, W. Klopper, and T. Helgaker, *Electron correlation: the many-body problem at the heart of chemistry*, J. Comput. Chem. **28**, 1307 (2007)

Chapter 3

The Hartree–Fock theory

3.1 The Hartree–Fock approximation

In the *Hartree–Fock approximation* (HF), the electronic wave function is approximated by a single Slater determinant, and the energy is optimized with respect to variations of these spin-orbitals.

3.1.1 The HF wave function

In the HF framework, the approximate wave function may be written in a form

$$|\boldsymbol{\kappa}\rangle = \exp(-\hat{\kappa})\,|0\rangle\,, \tag{3.1}$$

where $|0\rangle$ is some reference configuration and $\exp(-\hat{\kappa})$ an operator that carries out unitary transformations among the spin orbitals; these orbital-rotation parameters for the Hartree–Fock ground state are obtained by *minimizing the energy*:

$$E_{\mathrm{HF}} = \min_{\boldsymbol{\kappa}} \left\langle \boldsymbol{\kappa} \left| \hat{H} \right| \boldsymbol{\kappa} \right\rangle . \tag{3.2}$$

The optimization could be carried out using standard numerical analyisis; however, for the most of purposes more "spesific" methods are required in order to cope with the computational cost.

3.1.2 The HF equations and the Fock operator

We recall that the Slater determinant represents a situation where electrons behave as independent particles, but are subject to the Fermi correlation. Therefore, the optimal determinant can be found by solving a set of effective one-electron Schrödinger equations – the *Hartree–Fock equations* – for the spin-orbitals, with the associated Hamiltonian being the *Fock operator*

$$\hat{f} = \sum_{PQ} f_{PQ} a_P^\dagger a_Q, \tag{3.3}$$

where the elements f_{PQ} are called the *Fock matrix*. A very essential feature of the Fock operator is that the one-electron part of the "true" molecular Hamiltonian is retained, but the two-electron part is replaced with the effective *Fock operator*, so that $\hat{f} = \hat{h} + \hat{V}$. The Fock operator incorporates *in an average sense* the Coulomb interaction among the electrons, corrected for Fermi correlation:

$$\hat{V} = \sum_{PQ} V_{PQ} a_P^\dagger a_Q \tag{3.4}$$

$$V_{PQ} = \sum_{I} \left(g_{PQII} - g_{PIIQ} \right), \tag{3.5}$$

where the integrals g are given in Eq. (A.33), with I running over the occupied and P and Q all spin-orbitals. The first term in V_{PQ} describes the classical Coulomb interaction of the electron with the charge distribution caused by the others, and the second one, *exchange term*, is a correction that arises from the antisymmetry of the wave function.

3.1.3 Self-consistent field method

The Hartree–Fock equations are solved by diagonalizing the Fock matrix. The resulting eigenvectors are called the *canonical spin-orbitals* and the the eigenvalues of the Fock matrix are the *orbital energies*, $f_{PQ} = \delta_{PQ}\epsilon_P$.

Since the Fock matrix is defined in terms of its own eigenvectors, the canonical spin-orbitals and the orbital energies can only be obtained using an *iterative procedure*; where the Fock matrix is constructed and diagonalized in every iteration until the spin-orbitals obtained in a particular iteration become identical to those from which the Fock matrix was constructed. This procedure is referred to as the *self-consistent field* (SCF) method and the resulting wave function the *SCF wave function*.

In the *canonical representation*, i.e., in the frame where the Fock matrix is diagonal, the electrons occupy the spin-orbitals in accordance with the Pauli principle and move independently one another in the electrostatic field caused by the stationary nuclei and by the charce distribution of the $N-1$ electrons. The orbital energies are the one-electron energies associated with the independent electrons and may thus be interpreted as the *energies required to remove a single electron*, that is, to ionize the system.

The identification of the orbital energies with the negative ionization potentials is known as the *Koopman's theorem*.

The Hartree–Fock state is invariant to unitary transformations among the occupied spin-orbitals. Therefore, the spin-orbitals of the Hartree–Fock state are not uniquely determied by the condition (3.2) and the canonical orbitals are just one possible choice of spin-orbitals for the optimized N-particle state. Any set of energy-optimized orbitals decomposes the Fock matrix into two non-interacting blocks: one for the occupied, and another for the unoccupied spin-orbitals. When these subblocks are diagonalized, the canonical spin-orbitals are obtained.

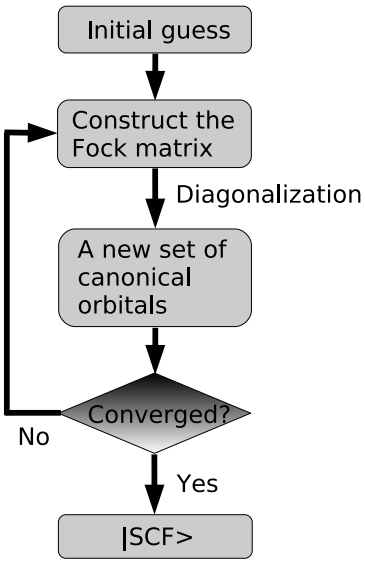


Figure 3.1: The self-consistent field procedure.

The final electronic state is obtained as an antisymmetrized product of the canonical spin orbitals

$$|\mathrm{HF}\rangle = \left(\prod_i a^\dagger_{i\alpha} a^\dagger_{i\beta} \right) |\mathrm{vac}\rangle \,. \tag{3.6}$$

Finally, let us make a remark that the Hartree–Fock state is an eigenfunction of the Fock operator with an eigenvalue equal to the sum of the orbital energies of the canonicial spin-orbitals

$$\hat{f}\,|\mathrm{HF}\rangle = 2 \sum_i \epsilon_i \,|\mathrm{HF}\rangle \,. \tag{3.7}$$

3.1.4 Restricted and unrestricted Hartree–Fock theory

The exact wave function is an eigenfunction of the total and projected spin operators. The Hartree–Fock wave function, which is not an eigenfunction of the Hamiltonian (but of the effective one, the Fock operator), does not possess these symmetries, they must be *imposed* on the Hartree–Fock solution.

- In the *restricted Hartree–Fock* (RHF) approximation, the energy is optimized subject to the condition that the wave function is an eigenfunction of the total and projected spins. In a practical implementation of the RHF scheme, it is advantageous to write the wave function as a configuration state function rather than a Slater determinant.

- In the *unrestricted Hartree–Fock* (UHF) approximation, the wave function is not required to be a spin eigenfunction, and different spatial orbitals are used for different spins.

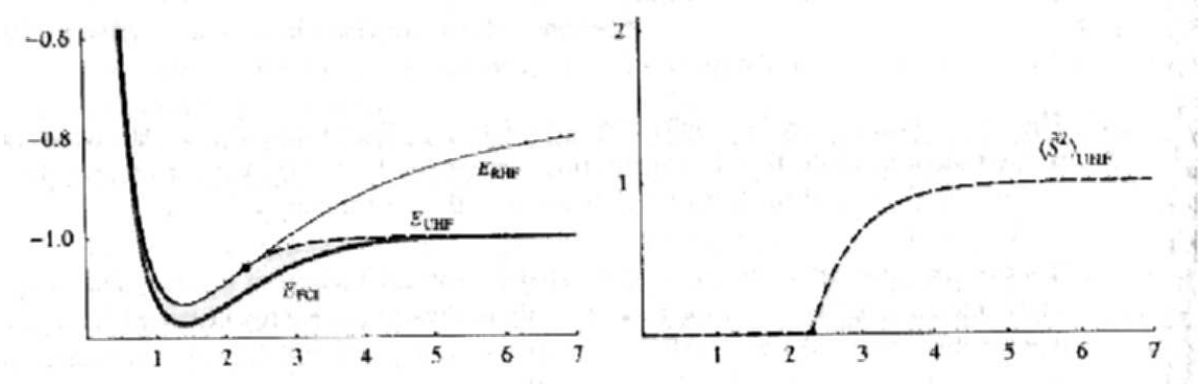
- In some systems, usually close to the equilibrium geometry, the symmetries of the exact state are present in the UHF state as well. In such cases the UHF and RHF states coincide.

3.1.5 Example: Hartree–Fock treatment of H_2

For the hydrogen molecule, the RHF wave function is a singlet spin eigenfunction with doubly occupied symmetry-adapted $1\sigma_g$ orbitals;

$$\begin{aligned} |\mathrm{RHF}\rangle &= a^\dagger_{1\sigma_g\alpha} a^\dagger_{1\sigma_g\beta} |\mathrm{vac}\rangle \\ |\mathrm{UHF}\rangle &= a^\dagger_{\phi_1\alpha} a^\dagger_{\phi_2\beta} |\mathrm{vac}\rangle \,. \end{aligned}$$

Let us plot these wave functions as well as the exact wave function for comparison using the LCAO approximation for the orbital basis:



At short internuclear distances the RHF and UHF wave functions are identical, providing a crude but reasonable representation of the potential energy surface. At larger separations, the RHF wave function behaves poorly for energy, whereas the UHF wave function falls towards the correct FCI curve. On the other hand, while the RHF wave function remains a true singlet at all distances, the UHF wave function behaves incorrectly with respect to the spin, yielding a spin intermediate of a singlet and a triplet. This effect is referred to as the *spin contamination*.

3.1.6 Roothaan–Hall equations

We will now consider the classical Roothaan–Hall formulation [8, 9] of the Hartree–Fock theory, in which the MOs are expanded in a set of AOs, $\phi_p = \sum_\mu \chi_\mu C_{\mu p}$, whose expansion coefficients $\mathbf{C}$ are used as the variational parameters.

The Hartree–Fock energy is the expectation value of the true molecular electronic Hamiltonian (A.62), and is given in the orbital basis by

$$E^{(0)} = \left\langle \mathrm{HF} \left| \hat{H} \right| \mathrm{HF} \right\rangle = \sum_{pq} h_{pq} D_{pq} + \frac{1}{2} \sum_{pqrs} g_{pqrs} d_{pqrs} \tag{3.8}$$

where

$$D_{pq} = \left\langle \mathrm{HF} \left| \hat{E}_{pq} \right| \mathrm{HF} \right\rangle \tag{3.9}$$

$$d_{pqrs} = \langle \mathrm{HF} \left| \hat{e}_{pqrs} \right| \mathrm{HF} \rangle . \tag{3.10}$$

For a closed-shell state, the only nonzero elements of (3.9) and (3.10) are

$$\begin{aligned} D_{ij} &= 2\delta_{ij} \\ d_{ijkl} &= D_{ij}D_{kl} - \frac{1}{2}D_{il}D_{kj} = 4\delta_{ij}\delta_{kl} - 2\delta_{il}\delta_{kj}, \end{aligned}$$

and thus the total Hartree–Fock energy is

$$E^{(0)} = 2\sum_i h_{ii} + \sum_{ij}(2g_{iijj} - g_{ijji}). \tag{3.11}$$

The energy must be optimized subject to the orthonormality of the MOs. We introduce the Hartree–Fock Lagrangian

$$L(\mathbf{C}) = E(\mathbf{C}) - 2\sum_{ij}\lambda_{ij}(\langle\phi_i \,|\phi_j\rangle - \delta_{ij})$$

and the variational conditions are written in terms of it as

$$0 = \frac{\partial L(\mathbf{C})}{\partial C_{\mu k}} = 4h_{\mu k} + 4\sum_j(2g_{\mu kjj} - g_{\mu jjk}) - 4\sum_j S_{\mu j}\lambda_{jk},$$

which gives the condition for the optimized Hartree–Fock state

$$f_{\mu k} = \sum_j S_{\mu j}\lambda_{jk}. \tag{3.12}$$

Since the multiplier matrix $\boldsymbol{\lambda}$ is symmetric (for real orbitals), it can be diagonalized by an orthogonal transformation among the occupied orbitals, $\boldsymbol{\lambda} = \mathbf{U}\boldsymbol{\epsilon}\mathbf{U}^T$, the Hartree–Fock energy being invariant to such transformations. The off-diagonal Lagrange multipliers may thus be eliminated by an orthogonal transformation to a set of occupied MOs that satisfy the canonical conditions. In the canonical basis, the variational conditions become

$$\sum_\nu f^{\mathrm{AO}}_{\mu\nu}C_{\nu k} = \epsilon_k \sum_\nu S_{\mu\nu}C_{\nu k}, \tag{3.13}$$

where the elements of the *AO Fock matrix* are

$$f^{\mathrm{AO}}_{\mu\nu} = h_{\mu\nu} + \sum_i(2g_{\mu\nu ii} - g_{\mu ii\nu}). \tag{3.14}$$

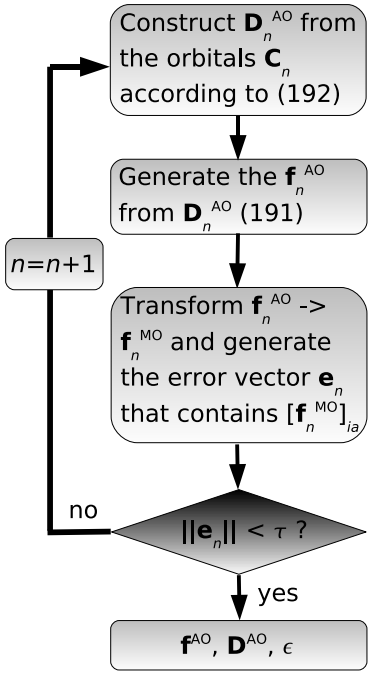


Figure 3.2: Roothaan–Hall procedure.

Since $\mathbf{f}^{\mathrm{AO}}$ is symmetric, we can extend the variational conditions to yield a set of orthonormal virtual MOs that satisfy the same canonical conditions as the occupied MOs, i.e., $f_{ab} = \delta_{ab}\epsilon_a$. Now, we are able to write the Hartree–Fock variational conditions as

$$\mathbf{f}^{\mathrm{AO}}\mathbf{C} = \mathbf{S}\mathbf{C}\boldsymbol{\epsilon}, \tag{3.15}$$

where $\boldsymbol{\epsilon}$ is a diagonal matrix that contains the orbital energies. This equation is called *the Roothaan-Hall equations*.

The AO Fock matrix can be evaluated entirely in the AO basis,

$$f_{\mu\nu}^{\mathrm{AO}} = h_{\mu\nu} + \sum_{\rho\sigma} D_{\rho\sigma}^{\mathrm{AO}} \left(g_{\mu\nu\rho\sigma} - \frac{1}{2} g_{\mu\sigma\rho\nu} \right), \tag{3.16}$$

where $\mathbf{D}^{\mathrm{AO}}$ is the AO representation of the one-electron density,

$$\mathbf{D}^{\mathrm{AO}} = \mathbf{C}\mathbf{D}\mathbf{C}^T. \tag{3.17}$$

3.2 Further topics in HF self-consistent field theory

3.2.1 On the convergence of the SCF method

A straightforward implementation of the Roothaan–Hall SCF method (given in the figure) may fail to converge or may converge slowly. Several schemes to improve the SCF

convergence have been introduced; of which the *direct inversion in the iterative subspace* (DIIS) method [10,11] is amongst the simplest and one of the most successful. In the DIIS method, the information from the preceding iterations is used instead of generating the next density from the last AO Fock matrix:

$$\bar{\mathbf{f}}_n^{\mathrm{AO}} = \sum_{i=1}^{n} w_i \mathbf{f}_i^{\mathrm{AO}}, \tag{3.18}$$

where the DIIS weights $\mathbf{w}$ are obtained by minimizing the norm of the averaged error vector $\bar{\mathbf{e}}_n = \sum_{i=1}^{n} w_i \mathbf{e}_i$,

$$\|\mathbf{e}\|^2 = \sum_{i=1}^{n}\sum_{j=1}^{n} w_i \underbrace{\langle \mathbf{e}_i \,|\mathbf{e}_j\rangle}_{B_{ij}} w_j,$$

subject to the constraint that $\sum_{i=1}^{n} w_i = 1$. For this purpose, we construct the Lagrangian

$$L = \sum_{i,j=1}^{n} w_i B_{ij} w_j - 2\lambda \left(\sum_{i=1}^{n} w_i - 1 \right),$$

the minimization of which leads to the set of linear equations:

$$\begin{pmatrix} B_{11} & B_{12} & \cdots & B_{1n} & -1 \\ B_{21} & B_{22} & \cdots & B_{2n} & -1 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ B_{n1} & B_{n2} & \cdots & B_{nn} & -1 \\ -1 & -1 & \cdots & -1 & 0 \end{pmatrix} \begin{pmatrix} w_1 \\ w_2 \\ \vdots \\ w_n \\ \lambda \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ -1 \end{pmatrix}$$

from which the weights are solved.

The C2-DIIS method [12] is similar to the DIIS, but the constraint is $\sum_{i=1}^{n} w_i^2 = 1$. This leads to a solution of an eigenvalue problem instead of the set of linear equations as in DIIS; the scheme may handle singularities better.

In the EDIIS ("energy DIIS") scheme [13], the error-vector-norm minimization is replaced by a minimization of an approximation to the true energy function. It improves the convergence in cases where the start guess has a Hessian structure far from the optimal one. It also can converge in cases where DIIS diverges. For non-problematic cases EDIIS has actually a slower convergence rate than DIIS.

These are based on either the diagonalization of the Fock matrix or on a direct optimization of the AO density matrix. Nevertheless, in some cases, even the DIIS method (and alike) is difficult to converge, when it might be better to use the second-order Newton method to the optimization of the Hartree–Fock energy. This has been applied in the literature to the optimization of the AO density matrix (the basis for the *trust-region* or *restricted-step method*) as well as in a method that carries out rotations among the MOs.

The "trust-region SCF" (TRSCF) [14] is basically a globally convergent black-box method, where each SCF iteration consists of a trust-region density subspace minimization and a trust-region Roothaan-Hall step.

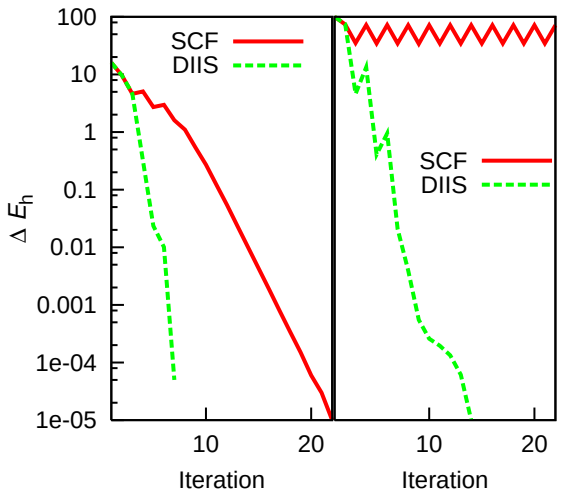


Figure 3.3: On the left: H_2O in its equilibrium geometry, on the right: H_2O with its bonds stretched to double (angle remaining constant). Calculations are carried out in the cc-pVQZ basis.

3.2.2 Integral-direct SCF

In every Roothaan–Hall SCF iteration a large number of two-electron integrals is needed to construct the Fock matrix. Since the same AO integrals are used in each iteration, these integrals can be written to disk and read in when needed.

In large-scale calculations, this approach becomes impractical due to the large number of needed integrals. In such cases, the AO integrals are instead recomputed in every iteration – as soon as a batch of two-electron integrals has been produced, it is contracted with the appropriate densities. This procedure is known as the *direct SCF* method [15].

If the value of an integral is very small, or if it is combined with small density-matrix elements, its contribution to the Fock matrix may be neglected. Therefore, by pre-estimating the integrals by having some kind of upper limit for them, the number of calculated integrals in the direct SCF scheme can be reduced dramatically. The computational cost of the SCF method scales formally as $\mathcal{O}(n^4)$, where n is the number of basis set functions, but it can be shown that only $\mathcal{O}(n^2)$ of the two-electron integrals are significant. Therefore, the direct SCF scheme combined with the pre-screening of the integrals is much cheaper for large systems.

3.2.3 Linear scaling aspirations

It is necessary to reduce the formal scaling of the models in order to apply them to larger molecular systems. This have been under intense study for many years, and significant progress have been achieved in the cases of SCF (and density-functional theory), which are based upon

- The *fast multipole method* [16]: the number of significant two-electron integrals scales

as $\mathcal{O}(N^2)$, but only $\mathcal{O}(N)$ have to be evaluated using the standard quantum-chemical means – the rest can be approximated by far simpler formulas. This applies to AOs whose overlap is close enough to zero.

- Linear scaling Fock-matrix construction: the contributions to the Fock matrix in the AO basis
$$f_{\mu\nu} = h_{\mu\nu} + \sum_{\rho\sigma} D^{\mathrm{AO}}_{\rho\sigma}(2g_{\mu\nu\rho\sigma} - g_{\mu\sigma\rho\nu}) \tag{3.19}$$
can be prescreened by the AO density matrix.

- Direct optimization of the density matrix [14]: the diagonalization step in the Roothaan–Hall SCF is avoided. These involve plenty of matrix-matrix multiplications, but the involved matrices are hoped to be sparse enough (in spatially large molecules) to allow $\mathcal{O}(N)$ evaluation of the multiplications.

3.3 Møller–Plesset perturbation theory

Finally, we consider less rigorous but computationally more appealing improvements of the Hartree–Fock description, based on perturbation theory. They are rather successful, when the Hartree–Fock wave function is reasonably accurate.

In *Møller–Plesset perturbation theory* (MPPT) [17, 18] the electronic Hamiltonian is partitioned as
$$\hat{H} = \hat{f} + \hat{\Phi} \tag{3.20}$$
where $\hat{f}$ is the Fock operator (3.3) and $\hat{\Phi}$ the *fluctuation potential*, which is the difference between the true two-electron Coulomb potential in $\hat{H}$ and the effective one-electron potential $\hat{V}$ of the Fock operator, $\hat{\Phi} = \hat{g} - \hat{V}$. The zero-order state is represented by the Hartree–Fock state in the canonical representation, that is $\hat{f}\,|\mathrm{HF}\rangle = \sum_I \epsilon_I\,|\mathrm{HF}\rangle$, and by applying the standard machinery of perturbation theory, we obtain to second order in the perturbation

$$E^{(0)}_{\mathrm{MP}} = \left\langle \mathrm{HF} \left| \hat{f} \right| \mathrm{HF} \right\rangle = \sum_I \epsilon_I \tag{3.21}$$

$$E^{(1)}_{\mathrm{MP}} = \left\langle \mathrm{HF} \left| \hat{\Phi} \right| \mathrm{HF} \right\rangle \tag{3.22}$$

$$E^{(2)}_{\mathrm{MP}} = -\sum_{A>B,I>J} \frac{|g_{AIBJ} - g_{AJBI}|^2}{\epsilon_A + \epsilon_B - \epsilon_I - \epsilon_J}. \tag{3.23}$$

Thus, the Hartree–Fock energy is equal to the sum of the zero- and first-order contributions; and by adding the second-order correction, we obtain the *second-order Møller–Plesset energy* (MP2)
$$E_{\mathrm{MP2}} = E_{\mathrm{HF}} - \sum_{A>B,I>J} \frac{|g_{AIBJ} - g_{AJBI}|^2}{\epsilon_A + \epsilon_B - \epsilon_I - \epsilon_J}, \tag{3.24}$$

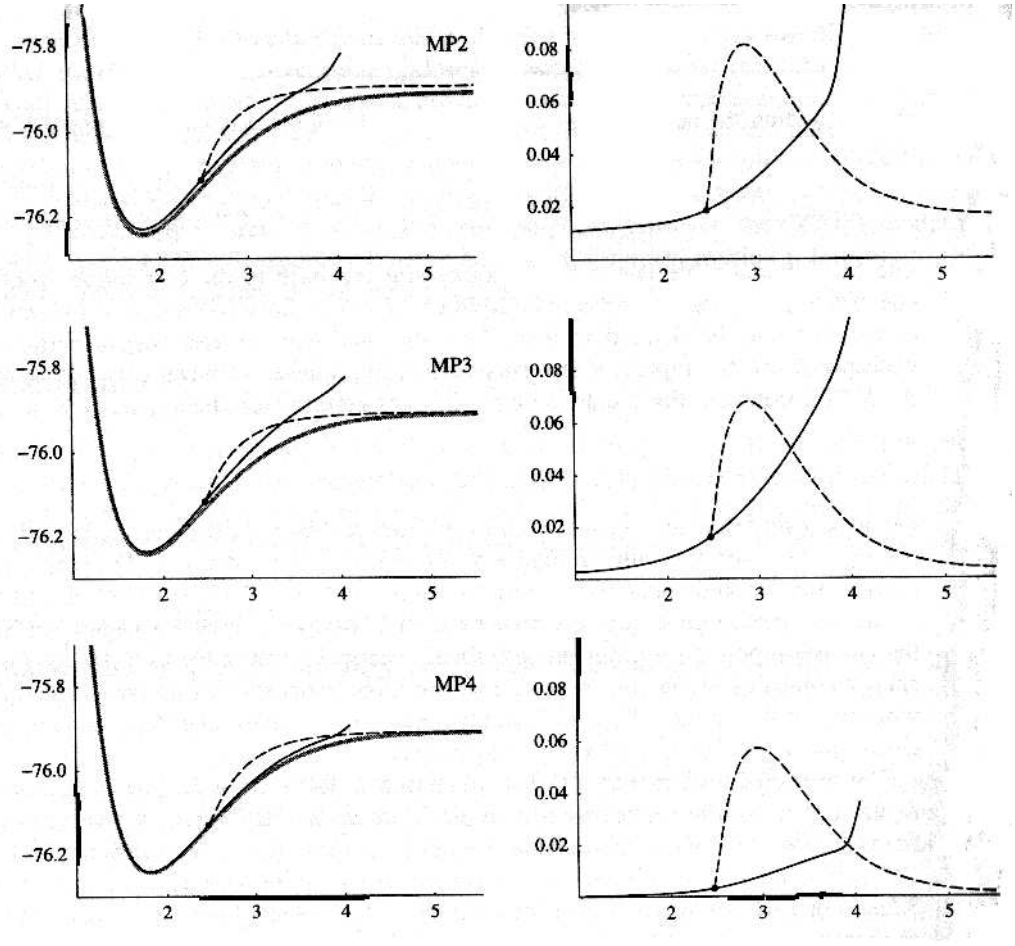


Figure 3.4: The MPn dissociation curves of the C_{2v} water molecule in the cc-pVDZ basis. Restricted MP2 with full and unrestricted with dashed line.

which is very popular and successful approach to introducing electron correlation on top of the Hartree–Fock wave function; providing surprisingly accurate and size-extensive correction at low computational cost. Higher-order corrections are derived in a similar manner, yielding MP3 and MP4 models, but these become rather expensive and are not as appealing compromise between cost and accuracy as MP2 is. Furthermore, the MPPT series have been shown to be inherently divergent.

3.4 Further reading

- T. Helgaker, P. Jørgensen, J. Olsen, *Molecular Electronic-Structure Theory* (Wiley 2002), pp. 433–522.
- J. Almlöf, *Notes on Hartree–Fock theory and related topics*, in B. O. Roos (ed), Lecture Notes in Quantum Chemistry II (Springer-Verlag 1994).

- J. Almlöf, *Direct methods in electronic structure theory*, in D. R. Yarkony (ed), Modern Electronic Structure Theory (World Scientific 1995), p. 110.

Chapter 4

Configuration interaction

4.1 Configuration-interaction wave function

The configuration-interaction (CI) wave function is constructed as a linear combination of Slater determinants (or configuration-state functions):

$$|\mathbf{C}\rangle = \sum_i C_i \, |i\rangle \tag{4.1}$$

with the coefficients determined by a variational optimization of the expectation value of the electronic energy, i.e., by minimization for the ground state

$$E_{\mathrm{CI}} = \min_{\mathbf{C}} \frac{\left\langle \mathbf{C} \middle| \hat{H} \middle| \mathbf{C} \right\rangle}{\langle \mathbf{C} \, | \mathbf{C} \rangle}. \tag{4.2}$$

As discussed earlier, this is equivalent to the solution of an eigenvalue equation $\mathbf{HC} = E_{\mathrm{CI}}\mathbf{C}$. The construction of the CI wave function may thus be carried out by diagonalizing the Hamiltonian matrix $H_{ij} = \left\langle i \middle| \hat{H} \middle| j \right\rangle$, but more often iterative techniques are used.

In particular, we have to construct the CI wave function in a finite one-electron basis. The *full CI* (FCI) wave function consists of all the configurations that can be generated in a given basis, and it is most convenient to think it as generated from a single reference configuration, which dominates the wave function and usually is the Hartree–Fock state, by the application of a linear combination of spin-orbital excitation operators

$$|\mathrm{FCI}\rangle = \left(1 + \sum_{AI} \hat{X}_I^A + \frac{1}{2} \sum_{ABIJ} \hat{X}_{IJ}^{AB} + \cdots \right) |\mathrm{HF}\rangle \, , \tag{4.3}$$

where for example

$$\begin{aligned} \hat{X}_I^A \, |\mathrm{HF}\rangle &= C_I^A a_A^\dagger a_I \, |\mathrm{HF}\rangle \\ \hat{X}_{IJ}^{AB} \, |\mathrm{HF}\rangle &= C_{IJ}^{AB} a_A^\dagger a_B^\dagger a_I a_J \, |\mathrm{HF}\rangle \, . \end{aligned}$$

	$R = R_{\text{ref}}$		$R = 2R_{\text{ref}}$	
	$E - E_{\text{FCI}}$	Weight	$E - E_{\text{FCI}}$	Weight
RHF	0.2178	0.9410	0.3639	0.5896
CISD	0.0120	0.9980	0.0720	0.9487
CISDT	0.0090	0.9985	0.0560	0.9590
CISDTQ	0.0003	1.0000	0.0058	0.9988
CISDTQ5	0.0001	1.0000	0.0022	0.9995

Thus, we may characterize the determinants in the FCI expansion as single (S), double (D), triple (T), quadruple (Q), quintuple (5), and so forth excitations relative to the Hartree–Fock state.

The number of determinants in an FCI wave function is

$$N_{\text{det}} = \binom{n}{k}^2 = \left(\frac{n!}{k!(n-k)!}\right)^2, \tag{4.4}$$

for a system with n orbitals containing k alpha and k beta electrons. For example, when $n = 2k$, $N_{det} \approx 16^k/k\pi$ – for large k, the number of determinants increases by a factor of 16 for each new pair of electrons and orbitals!

4.1.1 Single-reference CI wave functions

As the FCI wave function is obtainable only for the smallest systems, it becomes necessary to *truncate* the expansion, so that only a subset of the determinants are included, based on the excitation level. This is justified, since in general the lower-order excitations are more important than those of high orders. In principle, this procedure of *hierarchal truncation* may be continued until the FCI wave function is recovered. Since the CI model is variational, the FCI energy is approached from the above.

The electronic energies of truncated CI wave functions for the water molecule (cc-pVDZ basis) relative to the FCI energy:

Whereas the contributions drop monotonically, the step from an even-order excitation level to an odd-order is far more pronounced than the step from an odd to an even-order excitation level; hence the CI expansion is preferably truncated at even orders. For example, the first useful truncated CI wave function – the CI *singles-and-doubles wave function* (CISD) [19] – recovers 94.5% of the correlation energy, the inclusion of triples on top of that improves the treatment to 95.9%, while as much as 99.9% of the correlation energy is recovered at the CISDTQ level.

4.1.2 Multi-reference CI wave functions

In the stretched geometry $2R_{\text{ref}}$, the Hartree–Fock determinant is less dominant. Clearly, the strategy of defining a correlation hierarchy in terms of excitations out of a *single*

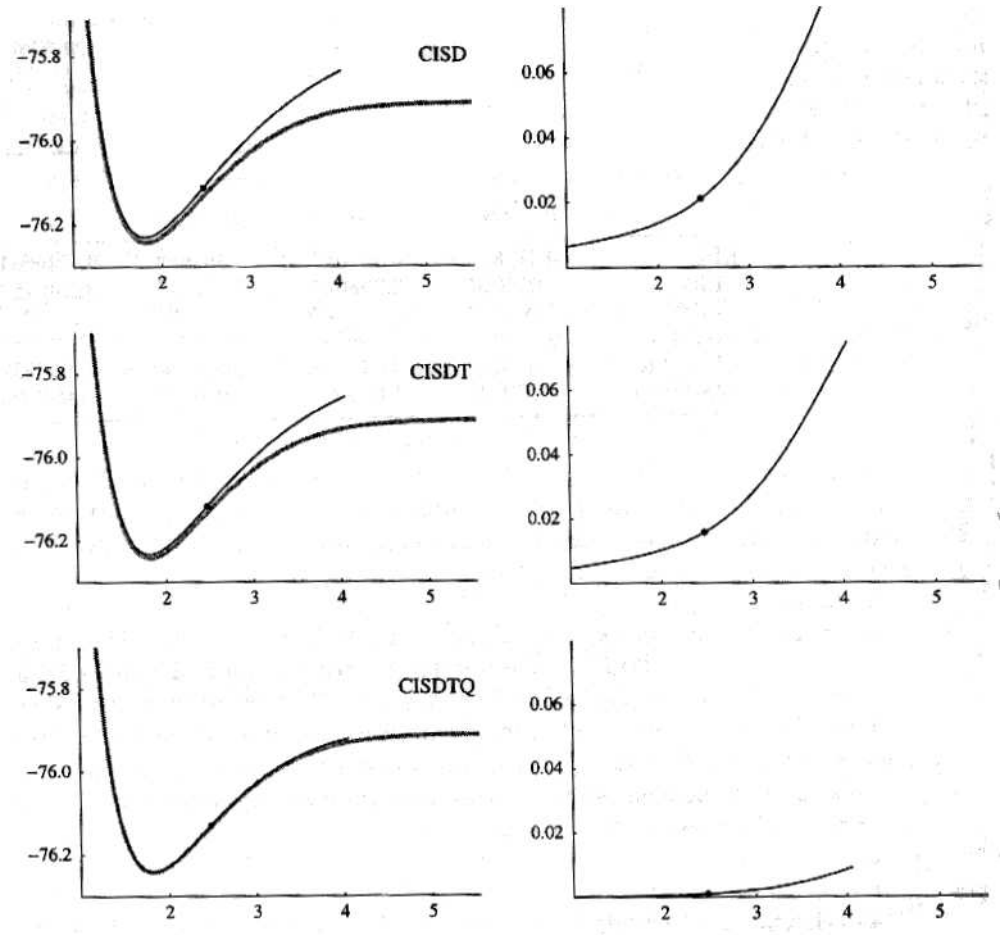


Figure 4.1: CI models

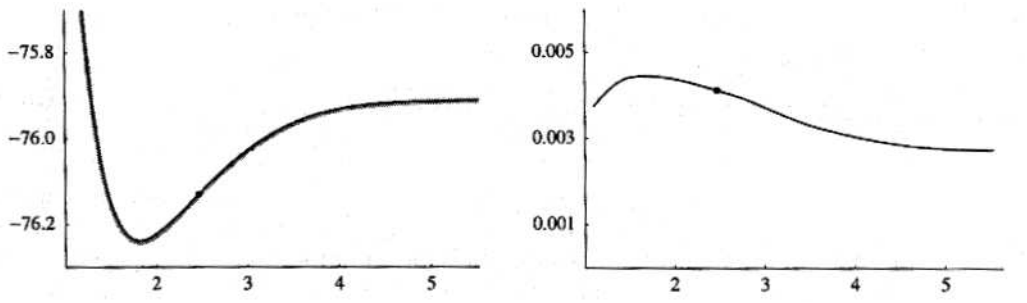


Figure 4.2: Performance of the MRSDCI model.

reference determinant such as the Hartree–Fock determinant does not provide the best possible description of the dissociation process. To overcome this, we may introduce CI wave functions based on the idea of a *reference space* comprising more than a single determinant: The *multi-reference CI* (MRCI) wave functions is generated by including in the wave function all configurations belonging to this reference space as well as all excitations up to a given level from each reference configuration, yielding, e.g., the multi-reference singles-and-doubles CI (MRSDCI) wave function.

The construction of a MRCI wave function begins with the generation of a set of orbitals and the reference space of configurations. For example, in the water molecule, we would include in our reference space for instance the configurations obtained by distributing the eight valence electrons among the six valence MOs in all possible ways (consistent with the spin- and space-symmetry restrictions).

- MRSDCI model is very accurate, if all the important configurations are included in the reference space.
- The number of important configurations becomes, however, very large, making thus the model applicable only to quite small systems.
- The choice of the active space requires a lot of chemical intuition and patience.

Another way of truncating the FCI expansion is to construct the wave function from *individual configurations*, the selection of which is based on physical intuition or perturbational estimates.

4.1.3 Optimization of the CI wave function

For large CI expansions it is impossible to set up and diagonalize the Hamiltonian matrix of the eigenvalue equation. However, usually only a few of the lowest eigenvalues are of interest, and we may determine them by *iterative methods*, where the eigenvectors and eigenvalues are generated by a sequence of linear transformations of the form $\boldsymbol{\sigma} = \mathbf{HC}$, where $\mathbf{C}$ is some trial vector. These methods can be devised for both of the CI eigenvalue problem and the optimization of the CI energy (4.2). The most often used strategies rely on the second-order Newton's method and its approximations.

4.1.4 On the disadvantages of the CI approach

CI wave functions truncated at a given excitation level relative to a reference configuration do not provide size-extensive energies.

- For example, if two fragments are described at the CISD level, then a size-extensive treatment of the compound system requires that the wave function is augmented with certain triples and quadruples; more precisely those that represent products of single and double excitations in the two subsystems.
- An approach called *quadratic CI* (QCI) is a size-extensive revision of the CI model. Other widely used approach to overcome the lack of size-extensivity is the *Davidson correction* applied on top of the truncated CI energy.

The CI description of the electronic system is not at all compact. Even though higher excitations are less important than those of lower orders, their number is enormous. Therefore, the CI wave function converges slowly with the number of variational parameters.

Both of these problems are due to the linear parameterization in the CI model (4.1).

4.2 Multi-configurational SCF theory

The multi-configurational self-consistent field (MCSCF) theory is a generalization of the Hartree–Fock wave function to systems dominated by more than one electronic configuration; that is, cases with pronouced static correlation. This method is particularly useful in the description of bond breakings and molecular dissociation processes.

4.2.1 MCSCF wave function

In MCSCF theory, the wave function is written as a linear combination of determinants, whose expansion coefficients C_i are optimized *simultaneously* with the MOs according to the variation principle:

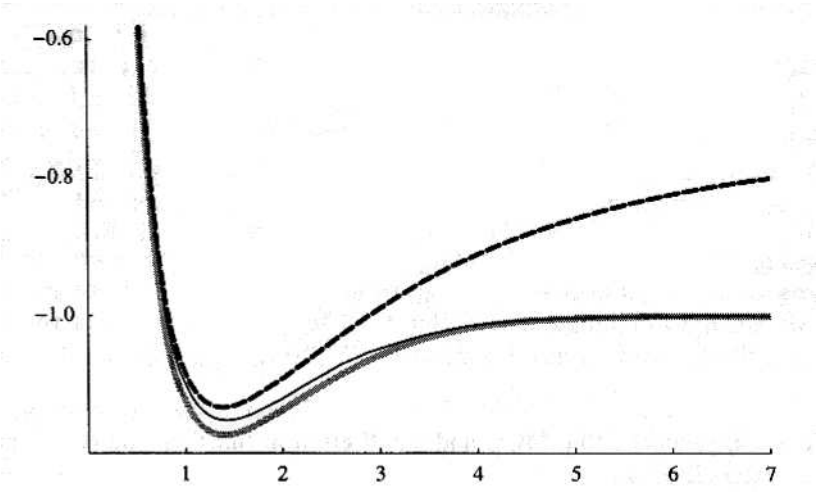
$$|\boldsymbol{\kappa}, \mathbf{C}\rangle = \exp(-\hat{\kappa}) \sum_i C_i \, |i\rangle \, . \tag{4.5}$$

The ground-state MCSCF wave function is obtained by minimizing the energy with respect to the variational parameters,

$$E_{\mathrm{MCSCF}} = \min_{\boldsymbol{\kappa},\mathbf{C}} \frac{\left\langle \boldsymbol{\kappa}, \mathbf{C} \middle| \hat{H} \middle| \boldsymbol{\kappa}, \mathbf{C} \right\rangle}{\langle \boldsymbol{\kappa}, \mathbf{C} \, | \boldsymbol{\kappa}, \mathbf{C} \rangle}. \tag{4.6}$$

4.2.2 Example: MCSCF wave function of H_2

A two-configuration MCSCF wave function of the hydrogen molecule is $|\mathrm{MC}\rangle = C_1 a^\dagger_{1\sigma_g\alpha} a^\dagger_{1\sigma_g\beta} \, |\mathrm{vac}\rangle + C_2 a^\dagger_{1\sigma_u\alpha} a^\dagger_{1\sigma_u\beta} \, |\mathrm{vac}\rangle$ where the variation principle is invoked to optimize the configuration



coefficients as well as the orbitals. The solid line is the potential energy curve in the cc-pVQZ basis set. The thick and the dashed lines are for FCI and RHF, respectively.

For any larger system than the H_2 molecule the selection of configuration space is the greatest difficulty in the MCSCF calculation. It is very often impossible to generate a sufficient MCSCF configuration, which is computationally tractable. The selection is usually carried out by dividing the MO space in *inactive*, *active*, and *secondary* orbitals.

- The inactive orbitals are set to be doubly occupied.
- The active orbitals have variable occupancies of 0, 1, or 2. The MCSCF expansion is then obtained by distributing the *active electrons* in all possible ways among the active orbitals. In the final optimized state, the active orbitals have non-integer occupation numbers between 0 and 2.
- The secondary orbitals are unoccupied throughout the optimization.

This scheme is called the *complete active space SCF method* (CASSCF) [20]. We note that the CASSCF wave function is identical to the FCI wave function, when all the orbitals of the system are active; and reduces to the Hartree–Fock wave function when the active space is empty.

In *restricted active space SCF* (RASSCF) [21, 22] calculations, the active orbital space is further divided into three subspaces: RAS1, with an upper limit on the allowed number of holes in each configuration; RAS2, with no restrictions enforced; and RAS3, with an upper limit on the allowed number of electrons in each configuration. This allows for larger active spaces than CASSCF.

In practice, the simultaneous optimization of orbitals and CI coefficients is a difficult nonlinear optimization problem, which restricts the MCSCF expansions to be significantly smaller than those encountered in the CI wave functions. By itself, the MCSCF model is not suited to the treatment of dynamical correlation, that requires large basis sets and long configuration expansions.

4.2.3 Example: Selection of the active space in H_2O

One popular approach for the choice of the MCSCF active spaces is based on the natural occupation numbers obtained from a preceding second-order Møller–Plesset perturbation theory calculation. For the water molecule in the cc-pVTZ basis in the order (A_1, B_1, B_2, A_2) we obtain

```
 Natural orbital occupation numbers, symmetry 1

        1.99953982     1.98393843     1.96476967     0.02261760     0.01156239
        0.00648257     0.00552982     0.00113424     0.00083070     0.00060446
        0.00047604     0.00036853     0.00035173     0.00019527     0.00013628
        0.00008516     0.00007619     0.00005837     0.00004768     0.00003078
        0.00002067     0.00001341     0.00000675

Natural orbital occupation numbers, symmetry 2

        1.96724668     0.01959000     0.00552930     0.00068405     0.00064037
        0.00042732     0.00035178     0.00013127     0.00005653     0.00004947
        0.00001646

Natural orbital occupation numbers, symmetry 3

        1.96415036     0.02452309     0.00641995     0.00104230     0.00086705
        0.00065869     0.00039618     0.00019746     0.00013435     0.00011930
        0.00006217     0.00005180     0.00003331     0.00001667     0.00001255
        0.00000755     0.00000429

Natural orbital occupation numbers, symmetry 4

        0.00626166     0.00079588     0.00038289     0.00012271     0.00006547
        0.00006019     0.00001431
```

We can choose active spaces of different flexibility:

- Smallest possible active space seems to be (2,0,2,0), i.e. four electrons in four MOs $3a_1$, $4a_1$, $1b_2$, and $2b_2$. This corresponds to a combination of 12 determinants.
- For more accurate description, eight electrons distributed on (3,1,2,0) active space, corresponding to 37 configurations, gives almost similar potential curve.
- For further improvement, an eight-electron (6,3,3,1) active space is of high quality and sufficient for incorporating dynamical correlation effects as well. However, we get almost the same curve by supplementing the CAS(3,1,2,0) wave function by RAS3 space (3,2,1,0) limiting the number of electrons in RAS3 space to be 2 at maximum. This reduces the number of determinants from 36240 to 2708.

4.3 Further reading

- I. Shavitt, *The Method of Configuration Interaction*, in H. F. Schaefer III (ed), Methods of Electronic-Structure Theory (Plenum Press 1977)

- H.-J. Werner, *Matrix-Formulated Direct Multiconfiguration Self-Consistent Field and Multiconfiguration Reference Configuration-Interaction Methods*, in K. P. Lawley (ed), Ab initio Methods in Quantum Chemistry (Wiley 1987)

Chapter 5

Coupled-cluster theory

5.1 Cluster expansion

5.1.1 Coupled-cluster wave function

As noted earlier, the shortcomings of the CI hierarchy – the lack of size-extensivity and the slow convergence towards the FCI limit – are due to the linear expansion.

However, we may recast the FCI expansion (4.3) in the form of a product wave function

$$|\mathrm{CC}\rangle = \left[\prod_{\mu}(1 + t_\mu \hat{\tau}_\mu)\right] |\mathrm{HF}\rangle \,, \tag{5.1}$$

where we have introduced a generic notation $\hat{\tau}_\mu$ for an excitation operator of unspecified excitation level (D, T, Q,...) and the associated *cluster amplitude* t_μ. This (full) *coupled-cluster (CC) wave function* differs from the FCI wave function by the presence of terms that are nonlinear in the excitation operators. Of course, the CC and FCI wave functions are completely equivalent provided that all the excitations are included.

Since the $\hat{\tau}$s always excite from the set of occupied Hartree–Fock spin-orbitals to the virtual ones, $[\hat{\tau}_\mu, \hat{\tau}_\nu] = 0$. Due to the presence of the product excitations in the coupled-cluster state (5.1), each determinant can thus be reached in several different ways. For example, the determinant $|\mu\nu\rangle = \hat{\tau}_\mu \hat{\tau}_\nu |\mathrm{HF}\rangle = \hat{\tau}_\nu \hat{\tau}_\mu |\mathrm{HF}\rangle$ may be reached with an overall amplitude equal to the sum of the individual amplitude. With respect to this determinant, the double-excitation amplitude $t_{\mu\nu}$ is referred to as a *connected cluster amplitude* and subsequent singles excitation amplitudes $t_\mu t_\nu$ as a *disconnected cluster amplitude*.

5.1.2 The CC Schrödinger equation

By analogy with the CI theory, we could attempt to determine the CC state by minimizing the expectation value of the Hamiltonian with respect to the amplitudes. Due to the nonlinear parameterization of the CC model, the analogous variational conditions would give rise to an intractable set of nonlinear equations. Hence, in practice *coupled-cluster*

models are not solved using the variation principle, and the CC energies are therefore non-variational.

Instead, by multiplying the eigenvalue equation $\hat{H}\left|\mathrm{CC}\right\rangle = E\left|\mathrm{CC}\right\rangle$ by $\langle\mu| = \langle\mathrm{HF}|\,\hat{\tau}_\mu^\dagger$ we obtain the *projected coupled-cluster equations*

$$\left\langle \mu \left| \hat{H} \right| \mathrm{CC} \right\rangle = E\left\langle \mu \,|\mathrm{CC}\right\rangle, \tag{5.2}$$

where the CC energy is obtained by projection against the Hartree–Fock state (note that $\langle\mathrm{HF}\,|\mathrm{CC}\rangle = 1$)

$$E = \left\langle \mathrm{HF} \left| \hat{H} \right| \mathrm{CC} \right\rangle. \tag{5.3}$$

These equations are nonlinear in amplitudes as well, but unlike the variational conditions, this expansion will, due to the Slater's rules (1.30-1.31), *terminate after few terms*, as we shall see later.

5.1.3 The coupled-cluster exponential ansatz

Because the excitation operators in (5.1) commute, i.e. $\hat{\tau}_\mu^2 = 0$, the correlating operators can be written in more convenient form, known as the *exponential ansatz for the coupled-cluster wave function*,

$$\left|\mathrm{CC}\right\rangle = \exp(\hat{T})\left|\mathrm{HF}\right\rangle, \tag{5.4}$$

where we have introduced the *cluster operator*

$$\hat{T} = \sum_\mu t_\mu \hat{\tau}_\mu. \tag{5.5}$$

In CC theory, a *hierarchy of approximations* is established by partitioning the cluster operator in the form

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots + \hat{T}_n, \tag{5.6}$$

where, for example,

$$\hat{T}_1 = \sum_{AI} t_I^A \hat{\tau}_I^A = \sum_{AI} t_I^A a_A^\dagger a_I \tag{5.7}$$

$$\hat{T}_2 = \sum_{A>B,I>J} t_{IJ}^{AB} \hat{\tau}_{IJ}^{AB} = \frac{1}{4}\sum_{AIBJ} t_{IJ}^{AB} a_A^\dagger a_I a_B^\dagger a_J. \tag{5.8}$$

Each excitation operator in $\hat{T}$ excites at least one electron from an occupied Hartree–Fock spin-orbital to a virtual one. It should be noted that for a system with N electrons, the expansion terminates after N terms. We further note that $[\hat{T}_i, \hat{T}_j] = 0$ as a trivial consequence of the individual excitation operator commutation relations. Moreover,

$$\begin{aligned} \langle\mathrm{HF}|\,\hat{\tau}_\mu &= 0 \\ \hat{\tau}_\mu^\dagger\left|\mathrm{HF}\right\rangle &= 0, \end{aligned}$$

because it is impossible to excite an electron from an unoccupied orbital.

To compare the CC model with the CI model, we expand the exponential operator and collect terms to the same order in excitation level:

$$\exp(\hat{T})\,|\mathrm{HF}\rangle = \sum_{i=0}^{N} \hat{C}_i\,|\mathrm{HF}\rangle\,.$$

The lowest-order operators $\hat{C}_i$ are given by

$$\begin{aligned}
\hat{C}_0 &= 1 \\
\hat{C}_1 &= \hat{T}_1 \\
\hat{C}_2 &= \hat{T}_2 + \frac{1}{2!}\hat{T}_1^2 \\
\hat{C}_3 &= \hat{T}_3 + \hat{T}_1\hat{T}_2 + \frac{1}{3!}\hat{T}_1^3 \\
\hat{C}_4 &= \hat{T}_4 + \hat{T}_3\hat{T}_1 + \frac{1}{2!}\hat{T}_1^2\hat{T}_2 + \frac{1}{4!}\hat{T}_1^4,
\end{aligned}$$

demonstrating the composition of the excitation processes. The advantages of the cluster parameterization arise in truncated wave functions and are related to the fact that even at the truncated level, the coupled-cluster state contains contributions from all determinants in the FCI wave function, with weights obtained from the different excitation processes.

5.1.4 Coupled-cluster model hierarchy

Similarly with the CI theory, a hierarchy of CC models is introduced by truncating the cluster operator at different excitation levels. The success of the models discussed below is illustrated in Figure 5.1.

The simplest successful CC wave function is the *coupled-cluster doubles* (CCD) model [23], where only the $\hat{T}_2$ operator is included to describe the electron-pair interactions.

For better accuracy the singles operator should be included too, yielding the *coupled-cluster singles-and-doubles* (CCSD) model [24]. In this model, the $\hat{T}_2$ operator describes the electron-pair interactions and $\hat{T}_1$ carries out the corresponding orbital relaxations. Its computational cost scales as $\mathcal{O}(N^6)$, similarly with CCD.

For higher accuracy, the connected triple excitations have to be taken into account, which leads to the *coupled-cluster singles-doubles-and-triples* (CCSDT) model. This model describes already the dynamical correlation almost perfectly, but is computationally very demanding, $\mathcal{O}(N^8)$ and is thus applicable to smallest molecules only.

The triples excitations can be estimated in a perturbational way, giving rise to the *CCSD(T) method* [25], which is a good compromise between the computational cost (exhibiting an $\mathcal{O}(N^7)$ scaling) and accuracy. It is often considered to be the best single-reference treatment of molecular Schrödinger equation that is applicable in practise.

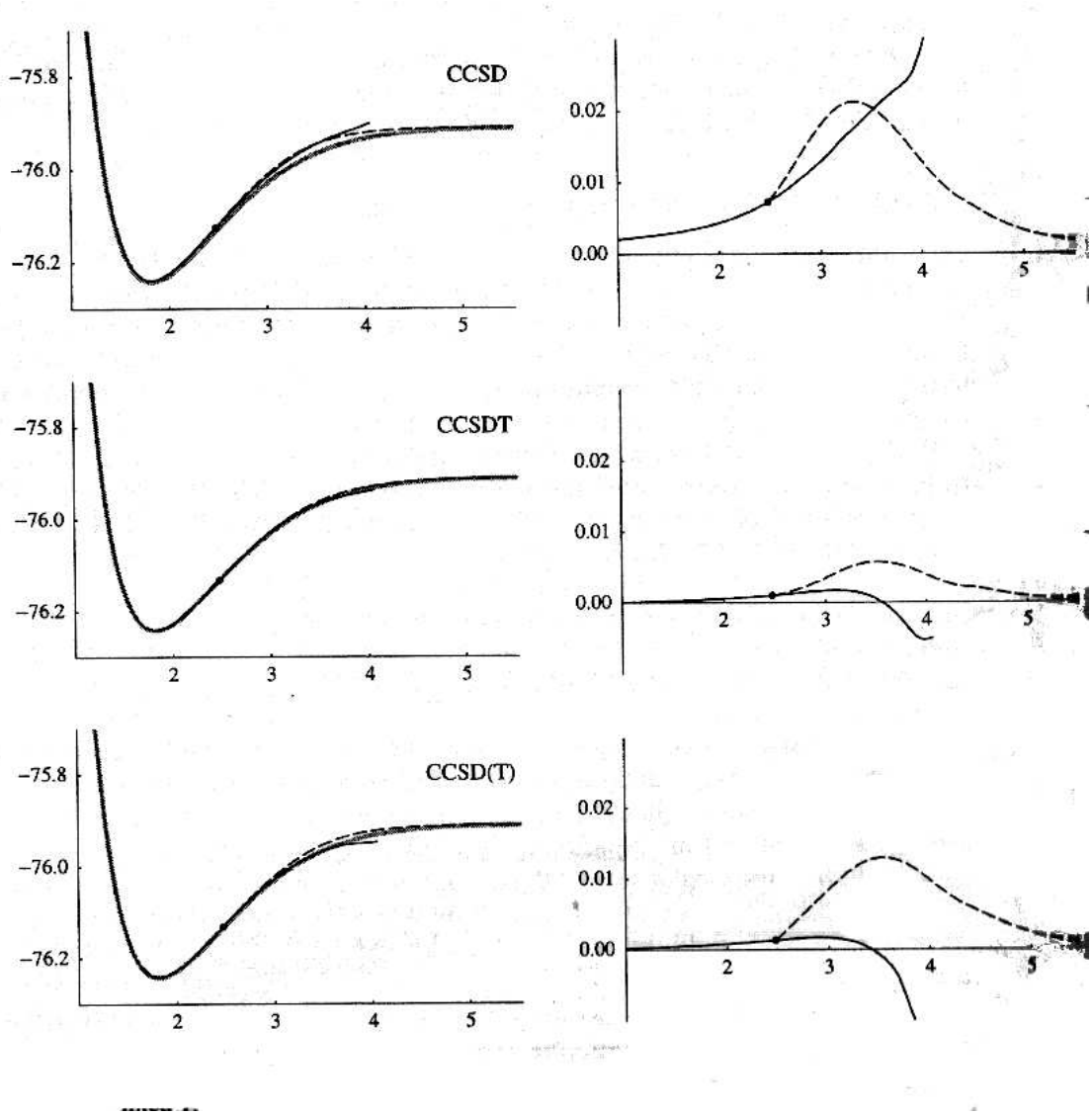


Figure 5.1: Success of the CC model hierarcy. On the left: The CC dissociation curves of the C_{2v} water molecule in the cc-pVDZ basis. On the right: corresponding differences between the CC and FCI energies. RHF reference state is plotted the full line and UHF with the dashed.

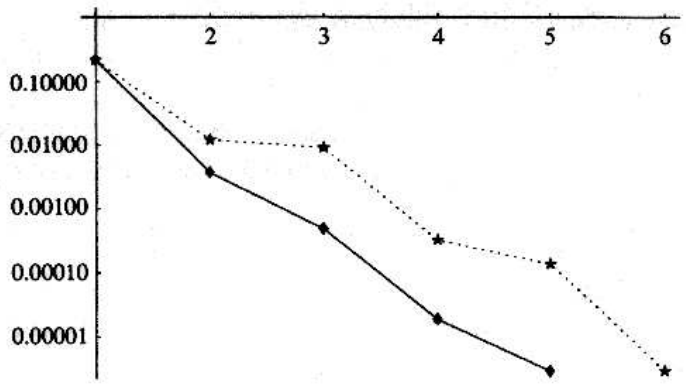


Figure 5.2: The error with respect to FCI of CC and CI wave functions as a function of the excitation level. Calculation for the water molecule at the equilibrium geometry in the cc-pVDZ basis.

5.1.5 CI and CC models compared

Let us at this point compare the CI and CC hierarchies; see Figure 5.2. Owing to the disconnected clusters, CC wave functions (full line) truncated at a given excitation level also contain contributions from determinants corresponding to higher-order excitations; whereas CI wave functions (dashed line) truncated at the same level contain contributions only from determinants up to this level. This is reflected in the convergence towards the FCI limit, which is typical of small systems.

A further notion outside the figure is that for larger systems, CI starts to behave very badly, while the CC description is unaffected by the number of electrons.

5.2 Solving the coupled-cluster equations

According to the previous discussion, the projected coupled-cluster equations are written as

$$\left\langle \mathrm{HF} \left| \hat{H} \exp(\hat{T}) \right| \mathrm{HF} \right\rangle = E \tag{5.9}$$

$$\left\langle \mu \left| \hat{H} \exp(\hat{T}) \right| \mathrm{HF} \right\rangle = E \left\langle \mu \left| \exp(\hat{T}) \right| \mathrm{HF} \right\rangle . \tag{5.10}$$

- The excited projection manifold $\langle \mu |$ comprises the full set of all determinants up to the chosen truncation level.
- For the full CC wave function, the number of equations is equal to the number of determinants and the solution of the projected equations recovers the FCI wave function.

- The nonlinear equations (5.9) must be solved iteratively, substituting in every iteration the CC energy calculated from (5.10).

It is convenient to rewrite the projected CC equations using the non-Hermitian *similarity-transformed Hamiltonian* $\hat{\bar{H}} = \exp(-\hat{T})\hat{H}\exp(\hat{T})$:

$$\left\langle \mathrm{HF} \left| \exp(-\hat{T})\hat{H}\exp(\hat{T}) \right| \mathrm{HF} \right\rangle = E \tag{5.11}$$

$$\left\langle \mu \left| \exp(-\hat{T})\hat{H}\exp(\hat{T}) \right| \mathrm{HF} \right\rangle = 0 \tag{5.12}$$

The equations (5.10) and (5.12) are completely equivalent (yet the equivalence is nontrivial for all the truncated CC models!), meaning that they yield same amplitudes and energy upon solution. They are referred to as the *unlinked* and *linked* coupled-cluster equations, respectively. Their computational cost is practically the same, but the linked equations have some advantages: Although both yield the same, size-extensive wave function, the linked equations are size-extensive *term by term*, that simplifies some perturbational treatments; in addition, the CC approach excited states in mind is more fruitful to start from the linked equations.

The main reason is however the following: When the Baker–Campbell–Hausdorff (BCH) expansion $\exp(\mathbf{A})\mathbf{B}\exp(-\mathbf{A}) = \mathbf{B} + [\mathbf{A},\mathbf{B}] + \frac{1}{2!}[\mathbf{A},[\mathbf{A},\mathbf{B}]] + \frac{1}{3!}[\mathbf{A},[\mathbf{A},[\mathbf{A},\mathbf{B}]]] + \cdots$ is applied to the similarity-transformed Hamiltonian, one obtains

$$\exp(-\hat{T})\hat{H}\exp(\hat{T}) = \hat{H} + [\hat{H},\hat{T}] + \frac{1}{2}[[\hat{H},\hat{T}],\hat{T}] + \frac{1}{6}[[[\hat{H},\hat{T}],\hat{T}],\hat{T}] + \frac{1}{24}[[[[\hat{H},\hat{T}],\hat{T}],\hat{T}],\hat{T}], \tag{5.13}$$

the coupled-cluster equations are therefore *no higher than quartic in the cluster amplitudes* – for any truncation level or even for full CC expansion.

Due to the Brillouin theorem, the one-particle operators contribute only to second order. Furthermore, cluster operators higher than the doubles do not contribute to the CC energy since $\hat{H}$ is a two-particle operator. As a result, only singles and doubles amplitudes contribute directly to the CC energy – irrespective of the truncation level of the cluster operator. Of course, the higher-order excitations contribute indirectly, since all amplitudes are coupled by the projected equations.

5.2.1 On coupled-cluster optimization techniques

The elements of the left-hand side of the CC amplitude equation (5.12) constitute the *coupled-cluster vector function* $\Omega_\mu(\mathbf{t})$, which can be expanded around the set of amplitudes of the current iteration $\mathbf{t}^{(n)}$:

$$\boldsymbol{\Omega}(\mathbf{t}^{(n)} + \Delta\mathbf{t}) = \boldsymbol{\Omega}^{(0)}(\mathbf{t}^{(n)}) + \boldsymbol{\Omega}^{(1)}(\mathbf{t}^{(n)}\Delta\mathbf{t} + \cdots,$$

where $\boldsymbol{\Omega}^{(0)}$ is the vector function calculated from the amplitudes $\mathbf{t}^{(n)}$ and $\boldsymbol{\Omega}^{(1)}$ the CC *Jacobian*

$$\Omega^{(1)}_{\mu\nu} = \left\langle \mu \left| \exp(-\hat{T}^{(n)})[\hat{H},\hat{\tau}_\nu]\exp(\hat{T}^{(n)}) \right| \mathrm{HF} \right\rangle. \tag{5.14}$$

Then an iterative scheme is established:

1. Solve the set of linear equations

$$\mathbf{\Omega}^{(1)}(\mathbf{t}^{(n)})\Delta\mathbf{t}^{(n)} = -\mathbf{\Omega}^{(0)}(\mathbf{t}^{(n)}) \tag{5.15}$$

   for $\Delta\mathbf{t}^{(n)}$

2. Form the improved estimate

$$\mathbf{t}^{(n+1)} = \mathbf{t}^{(n)} + \Delta\mathbf{t}^{(n)} \tag{5.16}$$

3. Iterate Equations (5.15) and (5.16) until convergence in the amplitudes.

In more sophisticated implementations, this Newton-method-like approach is replaced by a scheme, where the solution of the linear equations as well as the construction of the Jacobian are avoided by the approximation

$$\Delta t_\mu^{(n)} = -\varepsilon_\mu^{-1}\Omega_\mu^{(0)}(\mathbf{t}^{(n)}), \tag{5.17}$$

where, e.g. $\varepsilon_{ij}^{ab} = (\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j)$.

Usually, the convergence is accelerated by the DIIS method (see the discussion in section 3.1).

5.2.2 The closed-shell CCSD model

We consider now in detail the important special case of CC theory: the closed-shell CCSD model. We recall that the singlet CCSD state is generated by $|\mathrm{CC}\rangle = \exp(\hat{T}_1 + \hat{T}_2)\,|\mathrm{HF}\rangle$, hence only those terms in $\hat{T}_i$ that transform as singlet operators should be retained in the cluster operator. It is easy to show that

$$\left[\hat{S}_\pm, \hat{T}_i\right] = 0 \tag{5.18}$$

$$\left[\hat{S}_z, \hat{T}_i\right] = 0. \tag{5.19}$$

These impose important constraints on the cluster amplitudes in the spin-orbital basis. Due to these, the singles cluster operator becomes

$$\hat{T}_1 = \sum_{ai} t_i^a \hat{E}_{ai} \tag{5.20}$$

and the doubles operator

$$\hat{T}_2 = \frac{1}{2}\sum_{aibj} t_{ij}^{ab} E_{ai} E_{bj}. \tag{5.21}$$

The cluster amplitudes are symmetric: $t_{ij}^{ab} = t_{ji}^{ba}$.

The CCSD energy is obtained from Eq. (5.11). By noting that $\langle \mathrm{HF}| \exp(-\hat{T}) = \langle \mathrm{HF}|$, expanding the cluster operators and after some algebra we obtain the form

$$E_{\mathrm{CCSD}} = E_{\mathrm{HF}} + \frac{1}{2} \left\langle \mathrm{HF} \left| [[\hat{H}, \hat{T}_1], \hat{T}_1] \right| \mathrm{HF} \right\rangle + \left\langle \mathrm{HF} \left| [\hat{H}, \hat{T}_2] \right| \mathrm{HF} \right\rangle , \tag{5.22}$$

where the Hartree–Fock energy is given by $E_{\mathrm{HF}} = \left\langle \mathrm{HF} \left| \hat{H} \right| \mathrm{HF} \right\rangle$. By inserting the CCSD operators to the energy expression and calculating the commutators explicitly we obtain [26]

$$\begin{aligned} E_{\mathrm{CCSD}} &= E_{\mathrm{HF}} + \frac{1}{2} \sum_{aibj} t_i^a t_j^b \left\langle \mathrm{HF} \left| [[\hat{H}, \hat{E}_{ai}], \hat{E}_{bj}] \right| \mathrm{HF} \right\rangle + \frac{1}{2} \sum_{aibj} t_{ij}^{ab} \left\langle \mathrm{HF} \left| [\hat{H}, \hat{E}_{ai} \hat{E}_{bj}] \right| \mathrm{HF} \right\rangle \\ &= E_{\mathrm{HF}} + \frac{1}{2} \sum_{aibj} \left(t_{ij}^{ab} + t_i^a t_j^b \right) \left\langle \mathrm{HF} \left| [[\hat{H}, \hat{E}_{ai}], \hat{E}_{bj}] \right| \mathrm{HF} \right\rangle \\ &= E_{\mathrm{HF}} + \sum_{aibj} \left(t_{ij}^{ab} + t_i^a t_j^b \right) L_{iajb}, \end{aligned} \tag{5.23}$$

where we have denoted $L_{pqrs} = 2g_{pqrs} - g_{psrq}$.

5.3 Special formulations of coupled-cluster theory

5.3.1 The equation-of-motion coupled-cluster method

In CC theory, we arrive at a good description of the ground state. The excited states could be examined by carrying out separate, independent calculation for each state of interest, using in each case some appropriate zero-order reference determinant. However, it is usually difficult or even impossible to determine these adequate reference determinants; it is expensive to carry out individual calculations; and the states obtained in this manner are not orthogonal, which hinders the identification of the excited states.

Instead, we calculate the excited states in the spirit of CI theory, by a linear expansion in the space spanned by all states of the form

$$|\mathbf{c}\rangle = \sum_{\mu} c_\mu \hat{\tau}_\mu |\mathrm{CC}\rangle = \exp(\hat{T}) \sum_{\mu} c_\mu \hat{\tau}_\mu |\mathrm{HF}\rangle , \tag{5.24}$$

where the summation is carried out over all the excitation operators present in the cluster operator. This expansion is referred to as the *equation-of-motion coupled-cluster* (EOM-CC) model. The expansion parameters are optimized by the minimization of the energy

$$E(\mathbf{c}, \bar{\mathbf{c}}) = \frac{\left\langle \bar{\mathbf{c}} \left| \exp(-\hat{T}) \hat{H} \exp(\hat{T}) \right| \mathbf{c} \right\rangle}{\langle \bar{\mathbf{c}} \, | \mathbf{c} \rangle}. \tag{5.25}$$

The EOM-CC theory can be thought as conventional CI theory with a similarity-transformed Hamiltonian, which carries the information about electron correlation; while the configuration expansions carry the information about the excitation structure of the electronic states.

5.3.2 Orbital-optimized coupled-cluster theory

In the standard CC theory, we use the Hartree–Fock orbitals and then determine a set of non-zero single-excitation amplitudes together with higher-excitation amplitudes. Alternatively, we could use $\exp(\hat{T}_1)$ to generate an orbital transformation to a basis in which the single-excitation amplitudes vanish. This is the idea behind the *orbital-optimized (OCC) theory*, in which the orbital-rotation operator $\exp(-\hat{\kappa})$ is used instead of $\exp(\hat{T}_1)$ (as they generate the same state to first order),

$$|\mathrm{OCC}\rangle = \exp(-\hat{\kappa}) \exp(\hat{T}_O) |0\rangle \,, \tag{5.26}$$

where $\hat{T}_O = \hat{T}_2 + \hat{T}_3 + \cdots + \hat{T}_N$. The OCC energy is obtained in the usual manner by projecting the OCC Schrödinger equation against the reference state

$$E_{\mathrm{OCC}} = \left\langle 0 \left| \exp(-\hat{T}_O) \exp(\hat{\kappa}) \hat{H} \exp(-\hat{\kappa}) \exp(\hat{T}_O) \right| 0 \right\rangle , \tag{5.27}$$

whereas the cluster amplitudes are determined by projection against the manifold $|\mu_O\rangle$ spanned by $\hat{T}_O$

$$\left\langle \mu_O \left| \exp(-\hat{T}_O) \hat{H} \exp(-\hat{\kappa}) \exp(\hat{T}_O) \right| 0 \right\rangle = 0. \tag{5.28}$$

The *Brueckner coupled-cluster theory* (BCC) is closely related to OCC and differs in some details of the solution of orbital rotation parameters. Unlike in standard CC theory, the OCC and BCC orbitals are optimized simultaneously with the optimization of the cluster amplitudes – compare with the MCSCF theory. Surprisingly, the differences between standard and OCC/BCC wave functions are small. Only in the rare cases that are characterized by the sc. Hartree–Fock singlet instability the OCC/BCC are clearly more successful than the standard formulation.

5.3.3 Coupled-cluster perturbation theory

In the coupled-cluster perturbation theory (CCPT) [27] the Hamiltonian in the CC equations (5.11) and (5.12) is partitioned as in Eq. (3.20). The Fock and the cluster operator obey the following results:

$$\begin{aligned} \left[\hat{f}, \hat{T}\right] &= \sum_{\mu} \varepsilon_\mu t_\mu \hat{\tau}_\mu \\ \left[\left[\hat{f}, \hat{T}\right], \hat{T}\right] &= [[[\hat{f}, \hat{T}], \hat{T}], \hat{T}] = \cdots = 0. \end{aligned}$$

Thus we may write the non-Hermitian *similarity-transformed Fock operator* as

$$\hat{\bar{f}} = \hat{f} + \sum_{\mu} \varepsilon_\mu t_\mu \hat{\tau}_\mu, \tag{5.29}$$

and we arrive at the working equations of the CCPT:

$$E = E_0 + \left\langle \mathrm{HF} \left| \hat{\bar{\Phi}} \right| \mathrm{HF} \right\rangle \tag{5.30}$$

$$\varepsilon_\mu t_\mu = -\left\langle \mu \left| \hat{\bar{\Phi}} \right| \mathrm{HF} \right\rangle . \tag{5.31}$$

By expanding the cluster operator in the orders of the fluctuation potential we arrive at the amplitude equations

$$\varepsilon_\mu t_\mu^{(n)} = -\left\langle \mu \left| [\hat{\bar{\Phi}}]^{(n)} \right| \mathrm{HF} \right\rangle \tag{5.32}$$

where $[\hat{\bar{\Phi}}]^{(n)}$ contains the n^{th} order part of the similarity-transformed fluctuation potential. Then the amplitudes would be determined self-consistently from the projected equations after truncating the cluster operator at some excitation level. The CCPT is most often used to establish approximations to contributions from some excitations – the most famous is the non-iterative triples, or (T) correction to the CCSD wave function. Also very successful iterative CCPT schemes have been set up, e.g. the CC2 model approximates the CCSD model with the computational cost $\mathcal{O}(N^5)$ and CC3 the CCSDT model with the computational cost $\mathcal{O}(N^7)$. The CCPT series provides more systematic improvement to the wave function than the Møller–Plesset perturbation theory (MPPT).

In passing, we note that both MPPT and CCPT are limited to the ground states of systems dominated by a single configuration. To overcome this, *multiconfigurational perturbation theory* has been developed. Most important such theory is *CAS perturbation theory* (CASPT) [28], where the zero-order state is taken to be a CASSCF wave function. At the moment, it is the only generally applicable method for the *ab initio* calculation of dynamical correlation effects of open- and closed-shell multiconfigurational electronic system.

5.3.4 Local correlation methods

Linear scaling approximations for Hartree–Fock self-consistent field method are carried out almost routinely at the moment. However, linear scaling black-box correlated wave-function theory is far away from reality.

Traditional correlated electronic wave function methods, which are built upon the delocalized Hartree–Fock molecular orbitals (MO) do not exploit the fact that the electron correlation – i.e., the electron-electron Coulomb cusp – is spatially a rather local phenomenon.

In the recent literature, localized correlation methods have been pursued to overcome the "scaling wall" encountered in the correlated wave function methods. However, despite recent progress, there is still a need to formulate and implement new approaches that exploit the locality of the electron correlation problem. Approaches based on introducing locality in the correlation treatment using localized MOs (LMO) appeared already in 1960s and in the context of CC methods in 1980s [29, 30].

In the approach presented by Head-Gordon *et al.* CC equations are formulated in a general non-orthogonal [e.g., the atomic orbital] basis using a general tensor-based formulation [31]. Scuseria and Ayala presented a transformation of the standard MO CC doubles (CCD) equations into the AO basis [32,33]. Scuseria and Ayala argued that the solution of the CC equations in the AO basis scales in principle linearly with respect to N, but their approach seems so far not to have received any widespread use.

A fully operational local CCSD implementation have been presented by Werner *et al.* This implementation, referred to as the local CCSD (LCCSD) method [34–40], is based on localizing the occupied space as suggested by Pulay and coworkers [29], using traditional MO localization schemes, and using for the virtual space a projected atomic orbital (PAO) basis. LCCSD further relies on a spatial division of the system into domains. Restrictions on the extent to which the interactions between different domains are accounted for is important for achieving the low-power scaling of LCCSD making the results deviate from the standard CCSD results.

The equations of correlated wave function theories may also be derived in a biorthogonal PAO basis (thus without MOs altogether), aiming at a black-box formulation that could be applied to large systems [41, 42]. This formulation also constitutes a good platform to introduce efficient approximation schemes to reduce the number of parameters and thus the computational scaling. The locality of the PAO basis is reflected in the fact that the cluster amplitudes, the integrals as well as the correlation energy contributions decay exponentially with respect to the distance between the centers of the participating PAOs.

5.4 Further reading

- R. J. Bartlett, in *Modern Electronic Structure Theory* Vol II, edited by D. R. Yarkony (World Scientific, Singapore 1995).
- T. Helgaker, P. Jørgensen, and J. Olsen, *Molecular Electronic-Structure Theory* (Wiley 2002), pp. 648–816.
- T. J. Lee and G. E. Scuseria, in S. R. Langhoff (ed), *Quantum-Mechanical Electronic Structure Calculations with Chemical Accuracy* (Kluwer 1995).
- O. Christiansen, Coupled cluster theory with emphasis on selected new developments, Theor. Chim. Acta 116, 106 (2006).

Chapter 6

Basis sets and molecular integrals

6.1 Atomic basis functions

Molecular orbitals can be constructed either numerically or algebraically, of which the former provides greater flexibility and accuracy, but is tractable only for atoms and diatomic molecules; for polyatomic systems we are forced to expand the MOs $\phi_a(\mathbf{r})$ in a set of some simple analytical one-electron functions.

6.1.1 General considerations

Perhaps surprisingly, it turns out that the hydrogenic functions Eq. (1.13) are not ideal for this purpose; as they do not constitute a complete set by themselves but must be supplemented by the unbounded continuum states. Secondly, they become very diffuse and a large number of them is needed for a proper description of both the core and valence regions of a many-electron atom, especially when located in a molecule.

Therefore, in the molecular electronic-structure theory, χ's are usually functions of slightly more unphysical origin. Ideally, they should

1. allow orderly and systematic extension towards completeness with respect to one-electron square-integrable functions

2. allow rapid convergence to any atomic or molecular electronic state, requiring only a few terms for a reasonably accurate description of molecular electronic distributions

3. have an analytical form for easy and accurate manipulation especially for molecular integrals

4. be orthogonal or at least their non-orthogonality should not pose problems related to numerical instability.

6.1.2 Hydrogenic functions

Let us begin by reviewing the properties of the hydrogenic functions. As we noted earlier, they are the bounded eigenfunctions of the Hamiltonian

$$H = -\frac{1}{2}\nabla^2 - \frac{Z}{r}.$$

and are written as

$$\begin{aligned}\chi_{nlm}(r,\theta,\varphi) &= \underbrace{\left(\frac{2Z}{n}\right)^{3/2}\sqrt{\frac{(n-l-1)!}{2n(n+1)!}}\left(\frac{2Zr}{n}\right)^{l} L_{n-l-1}^{2l+1}\left(\frac{2Zr}{n}\right)\exp\left(-\frac{Zr}{n}\right)}_{R_{nl}(r)} \\ &\quad \times \underbrace{\sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta)\exp(\mathrm{i}m\varphi)}_{Y_{lm}(\theta,\varphi)}.\end{aligned}$$

The energy of the bounded hydrogenic state χ_{nlm} is given by

$$E_n = -\frac{Z^2}{2n^2}. \tag{6.1}$$

The degeneracy of the hydrogenic states of different angular momenta – that is, $2l+1$ degenerate states for every l – is peculiar to the spherical symmetry of the Coulomb potential and is lifted in a many-atom system. The notable features of the radial functions include

- the presence of the exponential
- that Laguerre polynomials introduce $n-l-1$ radial nodes in the wave function.

The diffusiveness of χ_{nlm} for large n is seen from the expectation value of $\hat{r}$

$$\langle \chi_{nlm} | \hat{r} | \chi_{nlm} \rangle = \frac{3n^2 - l(l+1)}{2Z} \tag{6.2}$$

In the following we consider basis functions that retain the product form of the hydrogenic wave functions but have a more compact radial part.

6.1.3 The Laguerre functions

In order to retain the correct exponential behavior but avoid the problems with continuum states we introduce the following class of functions:

$$\chi_{nlm}^{\mathrm{LF}}(r,\theta,\varphi) = R_{nl}^{\mathrm{LF}}(r)Y_{lm}(\theta,\varphi) \tag{6.3}$$

$$R_{nl}^{\mathrm{LF}} = (2\zeta)^{3/2}\sqrt{\frac{(n-l-1)!}{(n+l+1)!}}(2\zeta r)^l L_{n-l-1}^{2l+2}(2\zeta r)\exp(-\zeta r), \tag{6.4}$$

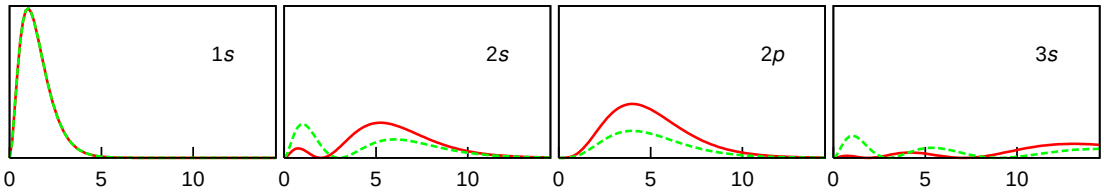


Figure 6.1: Lagurerre functions.

referred to as the *Laguerre functions*. For fixed l and ζ the radial functions (6.4) with $n > l$ constitute a complete orthonormal set of functions, for which

$$\left\langle \chi^{\mathrm{LF}}_{nlm} \left| \hat{r} \right| \chi^{\mathrm{LF}}_{nlm} \right\rangle = \frac{2n+1}{2\zeta}, \tag{6.5}$$

being thus considerably more compact than the hydrogenic functions for large n and independent of l. The Laguerre functions exhibit the same nodal structure as the hydrogenic ones but their radial distributions $R^2 r^2$ are quite different ($\zeta = 1/n$, $Z = 1$).

One should note that the orthogonality of the Laguerre functions is valid only with fixed exponents. It turns out, however, that the expansion of the orbital of a given l-value of an atomic system requires a large number of fixed-exponent Laguerre functions with different n. For non-orthogonal, variable-exponent functions Laguerre functions are not an optimal choice, but we need to introduce functions specifically tailored to reproduce as closely as possible the different orbitals of each atom.

6.1.4 Slater-type orbitals

In simplifying the polynomial structure of the Laguerre functions, we note that in R^{LF}_{nl} r occurs to power l and to powers $n-l-1$ and lower. Thus a nodeless one-electron function that resembles χ^{LF}_{nlm} and the hydrogenic functions closely for large r is obtained by retaining in the Laguerre function only the term of the highest power of r, yielding the *Slater-type orbitals* (STO)

$$\chi^{\mathrm{STO}}_{nlm}(r,\theta,\varphi) = R^{\mathrm{STO}}_{nl}(r) Y(\theta,\varphi) \tag{6.6}$$

$$R^{\mathrm{STO}}_{n}(r) = \frac{(2\zeta)^{3/2}}{\sqrt{\Gamma(2n+1)}} (2\zeta r)^{n-1} \exp(-\zeta r) \tag{6.7}$$

For the STOs we use the same $1s$, $2p$,... notation as for the hydrogenic functions, keeping in mind that STOs are *nodeless* and now n only refers to the monomial factor r^{n-1}. The expectation value of $\hat{r}$ and the maximum in the radial distribution curve are given by

$$\left\langle \chi^{\mathrm{STO}}_{nlm} \left| \hat{r} \right| \chi^{\mathrm{STO}}_{nlm} \right\rangle = \frac{2n+1}{2\zeta} \tag{6.8}$$

$$r^{\mathrm{STO}}_{\mathrm{max}} = \frac{n}{\zeta} \tag{6.9}$$

Also STOs would constitute a complete set of functions for a fixed exponent ζ, and we could choose to work with a single exponent and include in our basis orbitals ($1s$, $2s, \ldots$), ($2p$, $3p, \ldots$), ($3d$, $4d, \ldots$), all with the same exponent. Alternatively, we may describe the radial space by functions with *variable* exponents. For each l, we employ only the functions of the lowest n, yielding a basis of the type $((1s(\zeta_{1s}), 1s(\zeta_{2s}), \ldots), (2p(\zeta_{1p}, 2p(\zeta_{2p}), \ldots), \ldots)$ These variable-exponent STOs are given by

$$\chi_{\zeta_{nl}lm}(r,\theta,\varphi) = R^{\mathrm{STO}}_{\zeta_{nl}l}(r)Y_{lm}(\theta,\varphi) \tag{6.10}$$

$$R^{\mathrm{STO}}_{\zeta_{nl}l} = \frac{(2\zeta_{nl})^{3/2}}{\sqrt{(2l+2)!}}(2\zeta_{nl}r)^l \exp(-\zeta_{nl}r). \tag{6.11}$$

In practice, a combined approach is employed. For example, for the carbon atom, we would introduce sets of $1s$, $2s$ and $2p$ functions, all with variable exponents that are chosen to ensure an accurate representation of the wave function.

6.1.5 Gaussian-type orbitals

The STO basis sets are very successful for atoms and diatomic molecules, but the evaluation of many-center two-electron integrals becomes very complicated in terms of them. The basis sets that have established to be the standard practice in molecular electronic-structure theory are less connected to the hydrogenic functions or actual charge distributions in molecules. They are called *Gaussian-type orbitals* (GTO) as they employ the Gaussian distributions $\exp(-\alpha r^2)$ instead of the $\exp(-\zeta r)$ as in STOs. A large number of GTOs are needed to describe an STO (or an AO) properly, but this is more than compensated by a fast evaluation of the molecular integrals.

The *spherical-harmonic GTOs* are

$$\chi^{\mathrm{GTO}}_{nlm}(r,\theta,\varphi) = R^{\mathrm{GTO}}_{nl}(r)Y_{lm}(\theta,\varphi) \tag{6.12}$$

$$R^{\mathrm{GTO}}_{nl}(r) = \frac{2(2\alpha)^{3/4}}{\pi^{1/4}}\sqrt{\frac{2^{2n-l-2}}{(4n-2l-3)!!}}(\sqrt{2\alpha}r)^{2n-l-2}\exp(-\alpha r^2). \tag{6.13}$$

They form a complete set of nonorthogonal basis functions. In above, the double factorial function is

$$n!! = \begin{cases} 1 & n = 0 \\ n(n-2)(n-4)\cdots 2 & \text{even } n > 0 \\ n(n-2)(n-4)\cdots 1 & \text{odd } n > 0 \\ \frac{1}{(n+2)(n+4)\cdots 1} & \text{odd } n < 0 \end{cases} \tag{6.14}$$

The spatial extent of the GTOs are

$$\left\langle \chi^{\mathrm{GTO}}_{nlm} \left| \hat{r} \right| \chi^{\mathrm{GTO}}_{nlm} \right\rangle \approx \sqrt{\frac{2n-l-2}{2\alpha}} \tag{6.15}$$

$$r^{\mathrm{GTO}}_{\mathrm{max}} = \sqrt{\frac{2n-l-1}{2\alpha}} \tag{6.16}$$

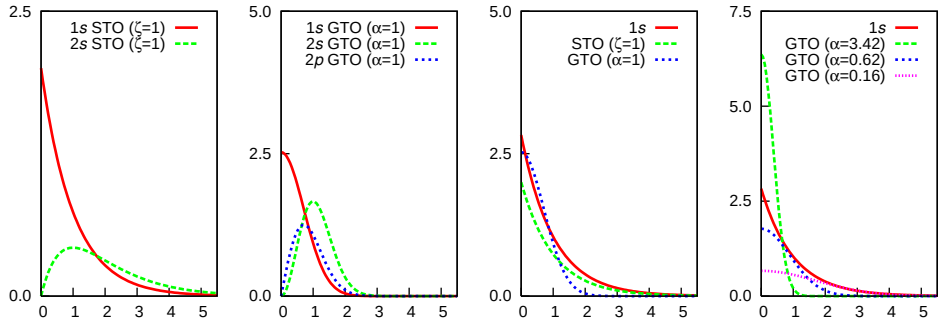


Figure 6.2: Slater and Gaussian-type orbitals compared.

When we compare these results with the case of STOs, we note that much larger number of GTOs are needed for a flexible description of outer regions of the electron distribution.

In practice, the use of GTOs with variable exponents differs from the procedure for STOs. For GTOs, we describe the radial space exclusively by means of variable exponents, using for this purpose only spherical-harmonic GTOs with $n = l + 1$, only powers of r introduced are thus associated with l of the spherical harmonics. The following set of spherical-harmonic GTOs is used:

$$\chi^{\mathrm{GTO}}_{\alpha_{nl}lm}(r,\theta,\varphi) = R^{\mathrm{GTO}}_{\alpha_{nl}l}(r)Y_{lm}(\theta,\varphi) \tag{6.17}$$

$$R^{\mathrm{GTO}}_{\alpha_{nl}l}(r) = \frac{2(2\alpha_{nl})^{3/4}}{\pi^{1/4}}\sqrt{\frac{2^l}{(2l+1)!!}}(\sqrt{2\alpha}r)^l \exp(-\alpha_{nl}r^2). \tag{6.18}$$

Let us finally consider the *Gaussian product rule*, that is the one of the main reasons why GTOs are so widely used. The product of two s GTOs $\chi_A = \exp(-\alpha r_A^2)$ and $\chi_B = \exp(-\beta r_B^2)$ centered on $\mathbf{r}_A$ and $\mathbf{r}_B$ is a third Gaussian

$$\chi_{AB} = \exp\left(-\frac{\alpha\beta}{\alpha+\beta}r_{AB}^2\right)\exp\left[-(\alpha+\beta)r_C^2\right] \tag{6.19}$$

centered on $\mathbf{r}_C$ given by

$$\mathbf{r}_C = \frac{\alpha\mathbf{r}_A + \beta\mathbf{r}_B}{\alpha+\beta}.$$

6.2 Gaussian basis sets

Of the three general features determining the accuracy of quantum chemical methods–the choice of the Hamiltonian, electron correlation treatment or truncation of the many-particle space, and the description of the one-particle space, i.e., the basis set used–the choice of the basis set is the most crucial one, as insufficient basis sets yield erroneous results regardless of the level of theory, whereas with a proper basis set, at least qualitatively correct results can be obtained for many problems already at the uncorrelated level of theory and using the non-relativistic Hamiltonian.

The majority of quantum chemical applications employ *contracted GTO* (CGTO) sets, i.e. linear combinations of GTO functions with coefficients optimized regarding some criterion (usually SCF energy) that significantly increase efficiency. There are two widely used contraction schemes: *segmented* contraction, where each GTO contributes only to a single CGTO, and *general* contraction, where such a restriction is not applied. Examples of the segmented scheme include the Pople-style basis set families (3-21G, 6-31G,...) [43, 44] and the Karlsruhe basis sets [45–47]. The correlation-consistent (cc) basis set families [48–53] by Dunning and co-workers are the most widely used generally contracted basis sets. The basic idea behind the cc sets is that functions that contribute approximately the same amount to the correlation energy are added to the basis in groups. The cc basis sets provide smooth, monotonic convergence for the electronic energy as well as for many molecular properties, especially those originating in the valence region. The polarized valence (cc-pVXZ, X = D, T, Q, 5, 6 corresponding to the number of CGTOs used to represent an occupied atomic orbital) and core-valence (cc-pCVXZ) sets can be augmented with diffuse functions (aug-cc-pVXZ and aug-cc-pCVXZ; d-aug-cc-pVXZ and t-aug-cc-pVXZ for doubly and triply augmented sets, respectively). While these features are favorable and the sets are widely used, the cc-basis sets become very large at large X, and it is not straightforward to extend the family beyond the published X values or to new elements. The atomic natural orbital (ANO) basis sets [54, 55] provide another general contraction approach. The contraction coefficients therein are atomic ANO coefficients that are obtained by optimizing atomic energies.

The use of increasingly large basis sets that produce results converging to some particular value is usually regarded as a solution to the problem of basis set incompleteness. In calculations of molecular properties that originate, e.g., in the region close to the nuclei (examples include indirect spin-spin couplings and hyperfine couplings), approaching the basis-set limit using the cc or comparable energy-optimized paradigms may lead to excessively large basis sets prohibiting calculations of large molecules. An alternative and often used approach is to uncontract the basis set and to supplement it by additional steep basis functions in the l-shells relevant for the property under examination.

The performance of the different basis sets for a certain molecular property can be qualitatively understood within a concept, which can be measured by the completeness profiles [56]

$$Y(\alpha) = \sum_m \langle g(\alpha)|\chi_m\rangle^2. \tag{6.20}$$

Here $\{\chi\}$ denotes a set of orthonormalized, contracted or primitive, basis functions, and $g(\alpha)$ is a primitive "test" GTO with the exponent α, used to probe the completeness of $\{\chi\}$. The completeness profile becomes unity for all α, for all l-values in a CBS. $Y(\alpha)$ is typically plotted in the logarithmic scale, against $x = \log\alpha$. In a certain exponent interval $[\alpha_{\min}, \alpha_{\max}]$ this quantity is intuitively connected to the possibility – from the point of view of one-particle space – of describing all details of the wave function in the corresponding distance range from the atomic nuclei. Put simply, atomic properties that obtain relevant contributions roughly within $[1/\sqrt{\alpha_{\max}}, 1/\sqrt{\alpha_{\min}}]$ from the nucleus can be

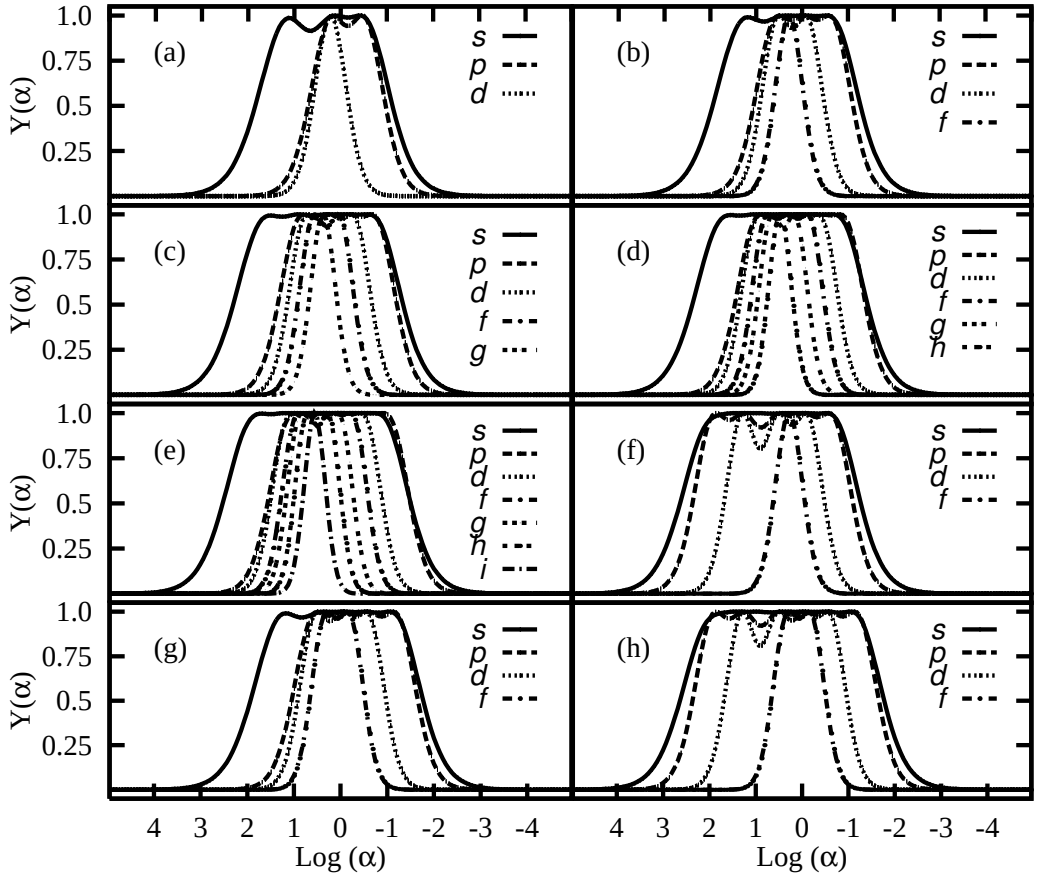


Figure 6.3: Completeness profiles of (a) cc-pVDZ (b) cc-pVTZ (c) cc-pVQZ (d) cc-pV5Z (e) cc-pV6Z (f) cc-pCVTZ (g) aug-cc-pVTZ and (h) aug-cc-pCVTZ basis sets of fluorine.

reproduced by a basis that has $Y(\alpha) = 1$ in this interval. This way of thinking can be generalized to molecular properties that may be dominated by phenomena occurring close to the expansion centers of the basis functions, i.e., atomic nuclei (region described by high-exponent basis functions) and/or in the valence region, further away from the nuclei. It has been later demonstrated that this property only can be the guiding factor for successful basis sets in form of the "completeness-optimized" basis sets [57].

6.3 Integrals over Gaussian basis sets

In the following, we will evaluate the one- and two-electron integrals

$$O_{\mu\nu} = \left\langle \chi_\mu \left| \hat{O} \right| \chi_\nu \right\rangle = \int \chi_\mu(\mathbf{r}) \hat{O}(\mathbf{r}) \chi_\nu(\mathbf{r}) d\mathbf{r} \tag{6.21}$$

$$\begin{aligned} O_{\mu\nu\lambda\sigma} &= \left\langle \chi_\mu(1)\chi_\nu(1) \left| \hat{O} \right| \chi_\lambda(2)\chi_\sigma(2) \right\rangle \\ &= \int \chi_\mu(\mathbf{r}_1)\chi_\nu(\mathbf{r}_1) \hat{O}(\mathbf{r}) \chi_\lambda(\mathbf{r}_2)\chi_\sigma(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \end{aligned} \tag{6.22}$$

such that the AOs (χ) are taken as fixed linear combinations of real-valued *primitive Cartesian GTOs*

$$G_{ijk}(\mathbf{r}, a, \mathbf{R}) = x_R^i y_R^j z_R^k \exp(-a r_R^2), \tag{6.23}$$

where the "Cartesian quantum numbers" i, j, k are greater than zero and $l = i + j + k$ for a given total angular momentum quantum number.

The integrals over primitive Cartesian GTOs may subsequently be transformed to integrals over contracted and/or spherical-harmonic GTOs (6.17) by linear combinations.

6.3.1 Gaussian overlap distributions

An important property of the primitive Cartesian GTOs is that they can be factorized in the three Cartesian directions,

$$G_{ijk}(\mathbf{r}, a, R) = G_i(x, a, R_x) G_j(y, a, R_y) G_z(z, a, R_z), \tag{6.24}$$

where for example $G_i(x, a, R_x) = x_R^i \exp(-a x_R^2)$. We will need also a concept of *Gaussian overlap distribution*

$$\Omega_{ab}(\mathbf{r}) = G_{ijk}(\mathbf{r}, a, \mathbf{R}_A) G_{lmn}(\mathbf{r}, b, \mathbf{R}_B), \tag{6.25}$$

that may also be factorized in the same way

$$\Omega_{ab}(\mathbf{r}) = \Omega_{ij}^x(x, a, b, R_{A,x}, R_{B,x}) \Omega_{kl}^y(y, a, b, R_{A,y}, R_{B,y}) \Omega_{mn}^z(z, a, b, R_{A,z}, R_{B,z}), \tag{6.26}$$

where the x component (for example) is given by

$$\Omega_{ij}^x(x, a, b, R_{A,x}, R_{B,x}) = G_i(x, a, R_{A,x}) G_j(x, b, R_{B,x}). \tag{6.27}$$

6.3.2 Simple one-electron integrals

We are now ready to consider simple one-electron integrals, by which we mean molecular integrals that do not involve the singular Coulombic $1/r$ interaction. All such integrals can be factorized in the three directions as

$$S_{ab} = S_{ij} S_{kl} S_{mn}. \tag{6.28}$$

According to the Gaussian product rule (6.19), any Cartesian component of the overlap distribution can be written as a single Gaussian at the centre of charge P_x, and we may thus evaluate the integral

$$\int_{-\infty}^{\infty} \Omega_{00}^{x} dx = \exp(-\mu X_{AB}^2) \int_{-\infty}^{\infty} \exp(-p x_p^2) dx = \sqrt{\frac{\pi}{p}} \exp(-\mu X_{AB}^2), \tag{6.29}$$

where μ denotes the reduced exponent $ab/(a+b)$, $p = a + b$, and

$$P_x = \frac{aR_{A,x} + bR_{B,x}}{p} \tag{6.30}$$

$$X_{AB} = R_{A,x} - R_{B,x}. \tag{6.31}$$

This result provides a basis for a set of *recurrence relations* by which we may evaluate simple integrals – overlap or more complicated ones – over GTOs of arbitrary quantum numbers. This procedure is known as *Obara–Saika scheme* [58, 59]. There exist other methods for molecular integral evaluation but we will not discuss them here. The relations are obtained by considering the behaviour of the integral under coordinate transformation and their detailed derivation is omitted here but recommended further reading.

The simplest case is the *overlap integral*

$$S_{ab} = \langle G_a \, | G_b \rangle \,, \tag{6.32}$$

for an Cartesian component of which the Obara–Saika relations are written as

$$S_{i+1,j} = X_{PA} S_{ij} + \frac{1}{2p}(i S_{i-1,j} + j S_{i,j-1}) \tag{6.33}$$

$$S_{i,j+1} = X_{PB} S_{ij} + \frac{1}{2p}(i S_{i-1,j} + j S_{i,j-1}). \tag{6.34}$$

For the linear and angular momentum as well as for kinetic energy integrals we need the integrals over differential operators

$$D_{ab}^{efg} = \left\langle G_a \left| \frac{\partial^e}{\partial x^e} \frac{\partial^f}{\partial y^f} \frac{\partial^g}{\partial z^g} \right| G_b \right\rangle. \tag{6.35}$$

In one direction the relations are

$$D_{i+1,j}^{e} = X_{PA} D_{ij}^{e} + \frac{1}{2p}(i D_{i-1,j}^{e} + j D_{i,j-1}^{e} - 2be D_{ij}^{e-1}) \tag{6.36}$$

$$D_{i+1,j}^{e} = X_{PB} D_{ij}^{e} + \frac{1}{2p}(i D_{i-1,j}^{e} + j D_{i,j-1}^{e} + 2ae D_{ij}^{e-1}), \tag{6.37}$$

with the $e = 0$ case providing the starting point and being equivalent with the overlap integral.

6.3.3 The Boys function

We will now introduce a special function that has a key role in the evaluation of one- and two-electron Coulomb integrals, the Boys function of order n, defined as

$$F_n(x) = \int_0^1 \exp(-xt^2)t^{2n}dt. \tag{6.38}$$

It is a strictly positive and decreasing function. We observe that the values of Boys function of order n at $x = 0$ have a closed-form expression

$$F_n(0) = \int_0^1 t^{2n}dt = \frac{1}{2n+1}. \tag{6.39}$$

Different methods for evaluating the Boys function has been introduced. One way is through recursion. By partial integration of the function we see that the different orders are related by

$$F_{n+1}(x) = (2n+1)F_n(x) - \exp(-x)2x \tag{6.40}$$

or

$$F_n(x) = 2xF_{n+1}(x) - \exp(-x)2n + 1. \tag{6.41}$$

We would therefore need to calculate the Boys function for the highest or the lowest order needed, and the others are obtained through the downward or upward recursion, of which the former is numerically more robust.

6.3.4 Obara–Saika scheme for one-electron Coulomb integrals

The Cartesian one-electron Coulomb integrals,

$$V_{ab} = \left\langle G_a \left| r_C^{-1} \right| G_b \right\rangle = \int \frac{\Omega_{ab}(\mathbf{r})}{r_C} d\mathbf{r}, \tag{6.42}$$

needed for the one-electron part of the molecular Hamiltonian, may also be evaluated by using the Obara–Saika recursion relations.

We again factorize the distribution according to (6.26), and are about to obtain the integrals through the recursion relations (c.f., below) for auxillary integrals Θ^N_{ijklmn}:

$$\begin{aligned}
\Theta^N_{i+1\,jklmn} &= X_{PA}\Theta^N_{ijklmn} + \frac{1}{2p}(i\Theta^N_{i-1\,jklmn} + j\Theta^N_{i\,j-1\,klmn}) \\
&\quad -X_{PC}\Theta^{N+1}_{ijklmn} - \frac{1}{2p}(i\Theta^{N+1}_{i-1\,jklmn} + j\Theta^{N+1}_{i\,j-1\,klmn}) \qquad (6.43) \\
\Theta^N_{i\,j+1\,klmn} &= X_{PB}\Theta^N_{ijklmn} + \frac{1}{2p}(i\Theta^N_{i-1\,jklmn} + j\Theta^N_{i\,j-1\,klmn}) \\
&\quad -X_{PC}\Theta^{N+1}_{ijklmn} - \frac{1}{2p}(i\Theta^{N+1}_{i-1\,jklmn} + j\Theta^{N+1}_{i\,j-1\,klmn}) \qquad (6.44)
\end{aligned}$$

with the special cases (that also serve the starting points of the recursion)

$$\Theta^0_{ijklmn} = V_{ijklmn} = V_{ab} \tag{6.45}$$

$$\Theta^N_{000000} = \frac{2\pi}{p} K^{xyz}_{ab} F_N(pR^2_{PC}), \tag{6.46}$$

where F_N is the Boys function, and we have denoted

$$K^x_{ab} = \exp(-\mu X^2_{AB}). \tag{6.47}$$

6.3.5 Obara–Saika scheme for two-electron Coulomb integrals

The evaluation of electron-electron repulsion integrals is a highly non-trivial task and due to their bottleneck status, under intense study since the early days of quantum chemistry. We will discuss here only one of the numerous schemes that is in accordance with the earlier discussion, namely the Obara–Saika scheme for Cartesian two-electron integrals,

$$g_{abcd} = \left\langle G_a(\mathbf{r}_1) G_b(\mathbf{r}_1) \left| r_{12}^{-1} \right| G_c(\mathbf{r}_2) G_d(\mathbf{r}_2) \right\rangle = \int\int \frac{\Omega_{ab}(\mathbf{r}_1)\Omega_{cd}(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2. \tag{6.48}$$

The relations feature similarly to the one-electron corresponds a set of auxillary integrals Θ. Again, two special cases of them are required:

$$\Theta^N_{0000\,0000\,0000} = \frac{2\pi^{5/2}}{pq\sqrt{p+q}} K^{xyz}_{ab} K^{xyz}_{cd} F_N(\alpha R^2_{PQ}) \tag{6.49}$$

$$\Theta^0_{i_x j_x k_x l_x\, i_y j_y k_y l_y\, i_z j_z k_z l_z} = g_{i_x j_x k_x l_x\, i_y j_y k_y l_y\, i_z j_z k_z l_z} = g_{abcd}. \tag{6.50}$$

In the above, we have denoted $K^{xyz}_{ab} = K^x_{ab} K^y_{ab} K^z_{ab}$ [c.f. Eq. (6.47)] and α is the reduced exponent $pq/(p+q)$. F_N is again the Boys function. In the following, the indices i, j, k and l are the Cartesian quantum numbers for orbitals a, b, c and d in the x-direction. Starting from these, first a set of integrals with $j = k = l = 0$ is generated by

$$\Theta_{i+1\,000} = X_{\mathrm{PA}} \Theta^N_{i000} - \frac{\alpha}{p} X_{\mathrm{PQ}} \Theta^{N+1}_{i000} + \frac{i}{2p} \left(\Theta^N_{i-1\,000} - \frac{\alpha}{p} \Theta^{N+1}_{i-1\,000} \right). \tag{6.51}$$

Then, the second electron is treated using the integrals generated in (6.51):

$$\Theta_{i0\,k+1\,0} = -\frac{bX_{\mathrm{AB}} + dX_{\mathrm{CD}}}{q} \Theta^N_{i0k0} - \frac{i}{2q} \Theta^N_{i-1\,0k0} + \frac{k}{2q} \Theta^N_{i0\,k-1\,0} - \frac{p}{q} \Theta^N_{i+1\,0k0}. \tag{6.52}$$

In the final step, the Cartesian powers are "transferred" between the orbitals of the same electron:

$$\Theta_{i\,j+1\,kl} = \Theta_{i+1\,jkl} + X_{\mathrm{AB}} \Theta^N_{ijkl} \tag{6.53}$$

$$\Theta_{ijkl+1} = \Theta_{ij\,k+1\,l} + X_{\mathrm{CD}} \Theta^N_{ijkl}. \tag{6.54}$$

In this way, we may construct the full set of Cartesian two-electron Coulomb integrals.

6.4 Further reading

- T. Helgaker and P. Taylor, *Gaussian basis sets and molecular integrals*, in Modern Electronic Structure Theory, Part II, D. R. Yarkony (ed.), (World Scientific 1995), pp. 725–856
- R. Lindh, *Integrals of electron repulsion*, in P. v. R. Schleyer et al. (eds.), Encyclopedia of Computational Chemistry Vol. 2, (Wiley 1998) p. 1337.

Chapter 7

Accounting for the effects of special relativity

7.1 Relativistic quantum mechanics

7.1.1 Theory of special relativity

In NR classical mechanics, two systems $\mathcal{O}$ and $\mathcal{O}'$ moving relative to one another with speed $\mathbf{v}$ are related with the Galileo transformation $\mathbf{x}' = \mathbf{x} + \mathbf{v}t$, with time t treated as an independent parameter. However, the famous Maxwell equations describing elecromagnetism are not invariant under Galileo transformation. This problem was culminated in the Michelson-Morley experiment, in which the speed of light was measured to be constant in all the directions of movement of the Earth. This was hard to explain with the classical theory, and the problem was solved in the theory of special relativity by Albert Einstein (1905), which is based on two postulates: 1. The laws of physics are the same in all inertial frames of reference, and 2. The speed of light in free space has the same value in all inertial frames of reference. These are satisfied in Lorentz transformation (1904) [1]

$$\mathbf{x}' = \gamma(\mathbf{x} - \mathbf{v}t) \tag{7.1}$$

$$t' = \gamma\left(t - \frac{\mathbf{v}\cdot\mathbf{x}}{c^2}\right) \tag{7.2}$$

where $\gamma = 1/\sqrt{1-(v/c)^2}$. The direct consequence of the theory of special relativity is that systems moving relative to each other with constant speed are equivalent, so no absolute reference system can exist.

7.1.2 Klein–Gordon equation

The straightforward relativistic analogue for the non-relativistic (NR) Schrödinger equation, $H\psi = i\partial\psi/\partial t$, using a relativistic energy-momentum relation, $E^2 = p^2c^2 + m^2c^4$, is

[1] Atomic unit system. In the four-algebra, the metric tensor $g_{\mu\nu} = \mathrm{diag}(1,1,1,-1)$. Einstein's summation convention is used.

the Klein-Gordon equation

$$-\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2}+\nabla^2\right)\psi = m^2c^2\psi. \tag{7.3}$$

The problem with the Klein-Gordon equation lies with the negative energy solutions that involve a negative probability density.

However, the equation is usable with re-interpreatation of the solutions – Pauli and Weisskopf interpreted the solution as a current density and Feynman and Stückelberg interpreted the negative energy solutions to describe either a particle moving backwards in time or an antiparticle moving forward in time. The Klein-Gordon equation is sufficient relativistic wave-equation for *spinless* paricles.

7.1.3 Dirac equation

To avoid these, Paul Dirac suggested a form of an equation [60, 61] that is linear in both $\partial/\partial t$ and ∇ as

$$H^{\text{Dirac}}\psi = (c\boldsymbol{\alpha}\cdot\mathbf{p}+\boldsymbol{\beta}mc^2)\psi, \tag{7.4}$$

where the factors $\boldsymbol{\alpha}_i$ $(i = 1, 2, 3)$ and $\boldsymbol{\beta}$ are defined by demanding that the relativistic energy-momentum relation be satisfied.

A comparison of Eq. (7.4) with the energy-momentum relation shows that $\boldsymbol{\alpha}_i$ and $\boldsymbol{\beta}$ anticommute and that $\boldsymbol{\alpha}_i^2 = \boldsymbol{\beta}^2 = \mathbf{1}$. $\boldsymbol{\alpha}_i$ and $\boldsymbol{\beta}$ are $N \times N$ matrices, with $N = 4$ being the lowest dimension that satisfies the equation. The equation can be written also in terms of larger N. The representation of $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ is not unambiguous. The Dirac-Pauli representation

$$\boldsymbol{\alpha}_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix}, \qquad \boldsymbol{\beta} = \begin{pmatrix} \mathbf{1} & 0 \\ 0 & -\mathbf{1} \end{pmatrix}, \tag{7.5}$$

where σ_i are the Pauli spin matrices

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \ \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \ \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{7.6}$$

is the most commonly used.

By multiplying (7.4) with $\boldsymbol{\beta}$ from left and denoting

$$\gamma_\mu = (-i\boldsymbol{\beta}\boldsymbol{\alpha}_k, \boldsymbol{\beta}), \ k = 1, 2, 3, \tag{7.7}$$

the resultant equation can be written into compact form as

$$(\gamma_\mu\partial_\mu + mc)\psi = 0, \tag{7.8}$$

where ∂_μ denotes differentation with respect to $x_\mu = (\mathbf{x}, ict)$. The gamma-matrices (7.7) can in fact be defined with condition $[\gamma_\mu, \gamma_\nu]_+ = 2g_{\mu\nu}$, and every four-matrices fulfilling this condition can be used as their representation. The representation corresponding to

Dirac-Pauli representation is the most common. This form of the the Dirac equation for a free electron can be shown to be Lorentz covariant and describe spin-half particles. The solution of the Dirac equation is a four-component Dirac spinor.

The solution also contains negative energy solutions, but with a positive probability density. They were interpreted as positrons, electrons with opposite charge. The positrons were experimentally observed a few years later [62]. The Dirac spinor can be divided into

$$\psi = \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix}, \tag{7.9}$$

where ψ_+ and ψ_- are the large- and small-component solutions. The solutions with large ψ_+ correspond mainly to the positive energy i.e. electronic solutions, whereas solutions with large ψ_- correspond to the positronic states.[2]

7.1.4 On the origin of magnetic energy levels

The substitution $p_\mu \to \pi_\mu = p_\mu - qA_\mu/c$, where A_μ is the 4-vector potential $(\mathbf{A}, -i\phi)$, yields the Dirac equation for a particle with charge q in the presence of an electromagnetic field,

$$\left[c\boldsymbol{\alpha} \cdot (\mathbf{p} - q\mathbf{A}/c) + q\phi + \boldsymbol{\beta}mc^2\right] \psi = i\partial_4 \psi. \tag{7.10}$$

For a constant magnetic field, the scalar potential $\phi = 0$ and the stationary state of the Eq. (7.10) this equation in terms of large and small components becomes

$$\begin{pmatrix} mc^2 & c\vec{\sigma} \cdot \boldsymbol{\pi} \\ c\vec{\sigma} \cdot \boldsymbol{\pi} & -mc^2 \end{pmatrix} \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} = E \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix}. \tag{7.11}$$

One obtains an equation involving only the upper components by solving for one pair in terms of the other,

$$\begin{aligned} \frac{(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})^2}{2m}\psi_+ &= \varepsilon\psi_+ \\ \Rightarrow \left(\frac{\pi^2}{2m} + \frac{q}{2mc}\boldsymbol{\sigma} \cdot \mathbf{B}\right)\psi_+ &= \varepsilon\psi_+. \end{aligned} \tag{7.12}$$

Here $\varepsilon = \frac{1}{2}(-mc^2 + E^2/mc^2)$ is approximately the energy of the particle minus the energy related to its mass. The first term is analogous to NR treatment of a charged particle in a magnetic field, which solutions $|n, k, m_l\rangle$ that are eigenfunctions of $H_{\rm nr}$, p_z, and L_z (L is the orbital angular momentum operator) with eigenvalues $p^2/2m + (2n+1)eB/2m$, p, and m_l, respectively. These are consistent with the classical picture of the charged particle moving in a helix with axis parallel to the field. The second term describes the interaction

[2]The non-relativistic limit ($c \to \infty$) of the Dirac equation, often referred to as the Lévy-Leblond equation [63], is a Galilei-invariant four-component equation that describes spin one-half particles. It describes correctly also the interaction between the electron spin and an external magnetic field, with the gyromagnetic ratio equalling to 2.

of the spin magnetic moment of the particle with the field. If the uniform field is chosen to be in x_3-direction in (7.12),

$$\begin{pmatrix} \frac{\pi^2}{2m} + \frac{q}{2mc}B & 0 \\ 0 & \frac{\pi^2}{2m} - \frac{q}{2mc}B \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \varepsilon \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix},$$

and hence either $\psi_1 \propto |n, k, m_l\rangle$ and $\psi_2 \equiv 0$ with $\varepsilon = (2n + 2)qB/2mc + p^2/2m$ or $\psi_2 \propto |n, k, m_l\rangle$ and $\psi_1 \equiv 0$ with $\varepsilon = neB/mc + p^2/2m$. ψ_+ is an eigenfunction of perpendicular part of the Hamiltonian with the field, p_3, L_3, and σ_3. The eigenvalue of the last is labeled as $2m_s$, which can be ± 1. The lower components are obtained from (7.11). The operator L_z does not commute with the Hamiltonian, and different components of the wavefunction are associated with different m_l values. However, it can be shown with a direct calculation that the operator

$$J_z = L_z + \frac{1}{2}\sigma_z \tag{7.13}$$

does commute with both the Hamiltonian and p_z, and hence the relativistic states are characterised by quantum numbers n, k, and m_j. The complete four-component functions are eigenfunctions of Dirac Hamiltonian with eigenvalues $E = \pm mc^2\sqrt{1 - \frac{2\varepsilon}{mc^2}}$,

$$\psi^+_{n,k,m_j} = C_+ \begin{pmatrix} |n-1, k, m_j - \frac{1}{2}\rangle \\ 0 \\ \frac{kc}{E_n + mc^2}|n-1, k, m_j - \frac{1}{2}\rangle \\ \frac{2c(\gamma n)^{1/2}}{E_n + mc^2}|n, k, m_j + \frac{1}{2}\rangle \end{pmatrix}, \tag{7.14}$$

$$\psi^-_{n,k,m_j} = C_- \begin{pmatrix} 0 \\ |n-1, k, m_j + \frac{1}{2}\rangle \\ \frac{2c(\gamma n)^{1/2}}{E_n + mc^2}|n, k, m_j + \frac{1}{2}\rangle \\ -\frac{kc}{E_n + mc^2}|n, k, m_j + \frac{1}{2}\rangle \end{pmatrix}. \tag{7.15}$$

Here $n = 1, 2, 3, \ldots$, k may obtain any value and m_j any half-integer value less or equal to $n - \frac{1}{2}$. When $n = 0$, only the second function is defined. The m_l and m_s are not defined in the fully relativistic picture, but they are for the large components. By introducing a quantum number $n' = n - \frac{1}{2}(|m_l| + m_l)$, the energy can be expressed as

$$\varepsilon = \frac{k^2}{2m} + \frac{q}{2mc}((2n' + |m_l|) + m_l + 2m_s)B \tag{7.16}$$

which expresses the contributions of the dipole-field interaction explicitly. Therefore, the quantised magnetic energy levels (Zeeman levels) arise naturally from Dirac theory.

7.2 Relativistic Hamiltonians for many-particle systems

7.2.1 Dirac–Coulomb Hamiltonian

As the essence of chemistry is a many-body quantum mechanical problem, it would be tempting to introduce a way of treating interacting electrons within the Dirac picture and hence obtain a proper description for the problem. The easiest way to construct a relativistic Hamiltonian for a many-electron system would be to include the potential terms that describe nucleus-electron and electron-electron Coulombic interactions,

$$H^{\mathrm{DC}} = \sum_i \left(H_i^{\mathrm{Dirac}} + \sum_K \frac{Z_K}{r_{iK}} \right) + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}, \tag{7.17}$$

The potentials of this Dirac-Coulomb Hamiltonian affect instantly, and hence H^{DC} is not Lorentz covariant.

7.2.2 Bethe–Salpeter equation

The Bethe–Salpeter equation [64, 65], which is essentially a generalisation of the Dirac equation for two particles, transforms properly under the Lorentz transformation. It is an integro-differential equation, which at least in principle can be made accurate to an arbitrarily high order. The derivation of the equation can be found from text books of relativistic quantum mechanics, and the equation in the most compact form is written as [66]

$$\begin{aligned} & \left(\gamma_\mu^{(1)} \partial_\mu + m^{(1)} c\right) \left(\gamma_\nu^{(2)} \partial_\nu^{(2)} + m^{(2)} c\right) \psi(x^{(1)}, x^{(2)}) \\ = & \int K(x^{(1)}, x^{(2)}, x^{(3)}, x^{(4)}) \psi(x^{(3)}, x^{(4)}) dx^{(3)} dx^{(4)}, \end{aligned} \tag{7.18}$$

where superscripts denote particles. The operator K includes Dirac matrix operators and x-dependent operators. The equation (7.18) can be written into different form separating space and time variables for each particle as

$$\left(D^{(1)} - i\partial_4^{(1)}\right) \left(D^{(1)} - i\partial_4^{(2)}\right) \psi = \mathcal{K}\psi, \tag{7.19}$$

where $D^{(i)}$ is the Dirac Hamiltonian for the free i^{th} particle [Eq. (7.4)], and $\mathcal{K}$ is $c^2 \boldsymbol{\beta}^{(1)} \boldsymbol{\beta}^{(2)}$ times the integral operator in (7.18). $\mathcal{K}$ can be derived from the quantum electrodynamics as a series valid to any order. The evaluation of $\mathcal{K}$ and t The solution of the resulting equation is problematic, in the use of the Bethe-Salpeter equation. In addition, and it features different time variables for the two particles. This is essential for the covariance but makes physical interpretation more difficult.

7.2.3 Dirac–Coulomb–Breit Hamiltonian

An approximate relativistic many-electron Hamiltonian can be constructed from the Dirac Hamiltonian by adding the Breit term [67]

$$H_{ij}^{\mathrm{Breit}} = -\frac{1}{r_{ij}}\left[\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j - \frac{(\boldsymbol{\alpha}_i \cdot \mathbf{r}_{ij})(\boldsymbol{\alpha}_j \cdot \mathbf{r}_{ij})}{2r_{ij}^2}\right] \tag{7.20}$$

that consists of the leading terms in the series obtained from the Bethe–Salpeter equation. It describes other pairwise additive interactions than the standard Coulomb interaction of electrons i and j, the first being the magnetic Gaunt term [68], and the second being a term that describes retardation, i.e. the finite speed of interaction. With this term, the Dirac–Coulomb–Breit (DCB) Hamiltonian is written as

$$H^{\mathrm{DCB}} = \sum_i H_i^{\mathrm{Dirac}} + \sum_{i,K}\frac{1}{r_{iK}} + \frac{1}{2}{\sum_{i,j}}'\frac{1}{r_{ij}} + \frac{1}{2}{\sum_{i,j}}' H_{ij}^{\mathrm{Breit}}. \tag{7.21}$$

It implicitly includes all relativistic effects on the kinetic energy as well as spin-orbit (SO) interaction. This Hamiltonian is, however, not Lorentz covariant, and it treats the effects of quantum electrodynamics perturbationally up to $\mathcal{O}(\alpha^2)$. Practical quantum chemistry with H^{DCB} is computationally too expensive for many purposes.

In addition, there are some theoretical defects in the DCB Hamiltonian, such as the Brown–Ravenhall disease [69], or the continuum dissolution, in which any bound multi-particle state is degenerate with a state containing negative energy continuum solutions. Another problem is related to the self-consistent field solution of the four-component equations [the Dirac–Fock(–Breit) method], in which solutions are obtained that not always are true upper bounds to the exact solution [70]. This is called the finite basis set disease. It can be at least partially treated using kinetic balance [71], which, however, leads to very large basis sets. These problems have kept applications of true chemical interest largely, but not completely, beyond the reach of rigorous four-component methods.

7.3 Quasi-relativistic Hamiltonians

Since chemistry is only concerned with the positive energy solutions of the Dirac equation, it would be useful to decouple the positive and negative energy components of (7.9) to give a two-component equation for the positive energy solutions, which could be used in the same manner as NR equations. There are several ways to reduce H^{DCB} into two-component form. Such approximate Hamiltonians are usually called *quasi-relativistic* Hamiltonians.

7.3.1 Foldy-Wouthuysen transformation

One way to decouple the large and small component solutions is to apply the Foldy-Wouthuysen transformation [72] (FW) on the Dirac Hamiltonian.

For an electron in potential V, when the zero-level of energy is chosen to be $+m_e c^2$, Eq. (7.11) is written as

$$\begin{pmatrix} V & c\vec{\sigma}\cdot\boldsymbol{\pi} \\ c\vec{\sigma}\cdot\boldsymbol{\pi} & V-2mc^2 \end{pmatrix} \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} = E \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix}.$$

Elimination of the small component (ESC) gives

$$\psi_- = \frac{c\vec{\sigma}\cdot\boldsymbol{\pi}}{2c^2+E-V}\,\psi_+ = \frac{1}{2c}\left(1+\frac{E-V}{2c^2}\right)^{-1}\vec{\sigma}\cdot\boldsymbol{\pi}\,\psi_+ \equiv \bar{X}\psi_+,$$

and therefore

$$H^{\mathrm{ESC}}\psi_+ \equiv V\psi_+ + c\vec{\sigma}\cdot\boldsymbol{\pi}\bar{X}\psi_+ = E\psi_+. \tag{7.22}$$

The Hamiltonian H^{ESC} is dependent on the energy E and operates on the unnormalised large component. In the normalised ESC approach [73], a normalised two-component wave function is generated, which affects the sc. picture change [74].

Foldy and Wouthuysen [72] introduced a systematic procedure, the Foldy-Wouthuysen (FW) transformation, for decoupling the large and small components to a successively higher order of c^{-1} by finding a unitary transformation that block-diagonalises the four-component Hamiltonian.

For a positive-energy two-component effective Hamiltonian, the transformation matrices

$$U = \begin{pmatrix} \frac{1}{\sqrt{1+X^\dagger X}} & \frac{1}{\sqrt{1+X^\dagger X}}X^\dagger \\ -\frac{1}{\sqrt{1+X^\dagger X}}X & \frac{1}{\sqrt{1+X^\dagger X}} \end{pmatrix}, \tag{7.23}$$

$$U^{-1} = U^\dagger = \begin{pmatrix} \frac{1}{\sqrt{1+X^\dagger X}} & -X^\dagger\frac{1}{\sqrt{1+X^\dagger X}} \\ X\frac{1}{\sqrt{1+X^\dagger X}} & \frac{1}{\sqrt{1+X^\dagger X}} \end{pmatrix} \tag{7.24}$$

generate the desired two-component FW wave function

$$\begin{pmatrix} \phi \\ 0 \end{pmatrix} = U \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix}. \tag{7.25}$$

When the energy-dependent $\bar{X}$ in Eq. (7.22) is expanded with respect to $(E-V)/2c^2$ to the lowest order, $X \approx (1/2c^2)c\vec{\sigma}\cdot\mathbf{p}$ is obtained, and to order c^{-2} in the absence of electromagnetic fields

$$U = \begin{pmatrix} 1-\frac{p^2}{8c^2} & \frac{c\vec{\sigma}\cdot\mathbf{p}}{2c^2} \\ -\frac{c\vec{\sigma}\cdot\mathbf{p}}{2c^2} & 1-\frac{p^2}{8c^2} \end{pmatrix}. \tag{7.26}$$

This, used with the FW transformation, gives rise to the Pauli Hamiltonian [75] (writing α instead of c^{-1}),

$$H^{\mathrm{Pauli}} = V + \frac{p^2}{2} - \frac{1}{8}\alpha^2(p^4-\nabla^2 V) + \frac{1}{4}\alpha^2\vec{\sigma}\cdot(\nabla V\times\mathbf{p}). \tag{7.27}$$

Here the first two terms correspond to the NR Hamiltonian. The third and the fourth term represent, respectively, the mass-velocity (mv) and Darwin (Dar) corrections that are often called the scalar relativistic (SR) corrections. The last term is the SO coupling term.

7.3.2 Breit-Pauli Hamiltonian

A two-component quasi-relativistic Hamiltonian for many-electron systems with the inclusion of the Breit term, i.e. the Breit-Pauli Hamiltonian, is gained from the Dirac-Coulomb-Breit Hamiltonian (7.21) for two-electron systems through the FW transformation and a generalisation to N electrons [1, 3, 66]. Omitting terms that describe the motion of the nuclei, the electronic part is written as

$$H^{\mathrm{BP}} = \sum_i h_i + \frac{1}{2}{\sum_{i,j}}' h_{ij}, \tag{7.28}$$

where the one-electron part is in the presence of electromagnetic fields

$$\begin{aligned}
h_i &= -\sum_K \frac{Z_K}{r_{iK}} && (7.29)\\
&+ \frac{1}{2}(\pi_i^2 + \mathrm{i}\vec{\sigma}_i \cdot \boldsymbol{\pi}_i \times \boldsymbol{\pi}_i) && (7.30)\\
&- \frac{1}{8}\alpha^2(\pi_i^2 + \mathrm{i}\vec{\sigma}_i \cdot \boldsymbol{\pi}_i \times \boldsymbol{\pi}_i)^2 && (7.31)\\
&+ \frac{1}{4}\alpha^2 \sum_K \frac{Z_K}{r_{iK}^3}\vec{\sigma}_i \cdot (\mathbf{r}_{iK} \times \boldsymbol{\pi}_i) && (7.32)\\
&+ \frac{\pi}{2}\alpha^2 \sum_K Z_K \delta(\mathbf{r}_{iK}). && (7.33)
\end{aligned}$$

Eq. (7.29) is the non-relativistic nuclear attraction potential, (7.30) describes non-relativistic kinematics and spin Zeeman interaction, term (7.31) is a relativistic correction to (7.30), (7.32) is the one-electron relativistic spin-orbit term, and (7.33) represents the one-electron Darwin effect. The two-electron part of the Breit-Pauli Hamiltonian consists of

$$\begin{aligned}
h_{ij} &= \frac{1}{r_{ij}} && (7.34)\\
&- \frac{1}{4}\alpha^2 \frac{\vec{\sigma}_i \cdot (\mathbf{r}_{ij} \times \boldsymbol{\pi}_i) - \vec{\sigma}_j \cdot (\mathbf{r}_{ij} \times \boldsymbol{\pi}_j)}{r_{ij}^3} && (7.35)\\
&- \pi\alpha^2 \delta(\mathbf{r}_{ij}) && (7.36)\\
&- \frac{1}{2}\alpha^2 \left[\boldsymbol{\pi}_i \cdot \frac{\boldsymbol{\pi}_j}{r_{ij}} + \frac{(\boldsymbol{\pi}_i \cdot \mathbf{r}_{ij})(\mathbf{r}_{ij} \cdot \boldsymbol{\pi}_j)}{r_{ij}^3}\right] && (7.37)\\
&- \frac{1}{2}\alpha^2 \frac{\vec{\sigma}_i \cdot (\mathbf{r}_{ij} \times \boldsymbol{\pi}_j) - \vec{\sigma}_j \cdot (\mathbf{r}_{ij} \times \boldsymbol{\pi}_i)}{r_{ij}^3} && (7.38)\\
&- \frac{1}{4}\alpha^2 \left[\frac{8\pi}{3}\delta(\mathbf{r}_{ij})(\vec{\sigma}_i \cdot \vec{\sigma}_j)\right.\\
&\quad \left. - \frac{(\vec{\sigma}_i \cdot \vec{\sigma}_j)}{r_{ij}^3} + \frac{3(\vec{\sigma}_i \cdot \mathbf{r}_{ij})(\vec{\sigma}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5}\right] && (7.39)
\end{aligned}$$

Here (7.34) is the Coulomb repulsion between the electrons, (7.35) the two-electron spin-same orbit term, (7.36) the two-electron Darwin term, (7.37) the orbit-orbit interaction, (7.38) the spin-other orbit interaction, and (7.39) the electronic spin-spin interaction.

We will in the following form an approximate electronic Hamiltonian for a molecule carrying a point-like nuclear magnetic dipole $\vec{\boldsymbol{\mu}}_K = \gamma_K \mathbf{I}_K$, where γ_K is the nuclear gyromagnetic ratio and $\mathbf{I}_K$ the nuclear spin, in external magnetic field $\mathbf{B}_0$, obtained by making a substitution $\boldsymbol{\pi} \to \mathbf{p} + \mathbf{A}$ into H^{BP}. This substitution and the corresponding expansion is presented in detail in Paper I. In this treatment, the vector potential $\mathbf{A}$ is expanded as a sum $\mathbf{A} = \mathbf{A}_0 + \mathbf{A}_K + \mathbf{A}_L$, where $\mathbf{A}_0$ is the vector potential corresponding to $\mathbf{B}_0$ in the Coulomb gauge $\nabla \cdot \mathbf{A} = 0$, and

$$\mathbf{A}_0(\mathbf{r}_i) = \frac{1}{2}\mathbf{B}_0 \times \mathbf{r}_{iO} \tag{7.40}$$

$$\mathbf{A}_K(\mathbf{r}_i) = \alpha^2 \gamma_K \frac{\mathbf{I}_K \times \mathbf{r}_{iK}}{r_{iK}^3} \tag{7.41}$$

are the fields caused by the point-like magnetic dipole moments of nuclei K and L. In Eq. (7.40), $\mathbf{r}_{iO} = \mathbf{r}_i - \mathbf{R}_O$, where O refers to the gauge origin. The terms containing a third or higher power in B_0 or a second or higher power in I_K or I_L are omitted. Explicit forms and physical interpretations of the obtained terms are presented in Tables 7.1, 7.3.2 and 7.3.2.

From the one-electron part, (7.30) is expanded as

$$\frac{1}{2}\sum_i \pi_i^2 \approx h^{\mathrm{KE}} + h_{B_0}^{\mathrm{OZ}} + h_K^{\mathrm{PSO}} + h_L^{\mathrm{PSO}} + h_{B_0^2}^{\mathrm{SUSC}} + h_{KB_0}^{\mathrm{DS}} + h_{LB_0}^{\mathrm{DS}} + h_{KL}^{\mathrm{DSO}} \tag{7.42}$$

for the NR kinematics. The NR spin Zeeman term [3] becomes

$$\frac{1}{2}\mathrm{i}\sum_i \vec{\sigma}_i \cdot (\boldsymbol{\pi}_i \times \boldsymbol{\pi}_i) = \frac{1}{2}\sum_i \vec{\sigma}_i \cdot \mathbf{B}_i = h_{B_0}^{\mathrm{SZ}} + h_K^{\mathrm{FC}} + h_L^{\mathrm{FC}} + h_K^{\mathrm{SD}} + h_L^{\mathrm{SD}}. \tag{7.43}$$

In (7.31), π_i^2 and $\mathrm{i}\vec{\sigma}_i \cdot \boldsymbol{\pi}_i \times \boldsymbol{\pi}_i$ do not commute when spatially non-uniform nuclear dipole fields are present, and thus the term is first expanded as

$$\begin{aligned} H_{\mathrm{kin}}^{\mathrm{R}} = & -\frac{1}{8}\alpha^2 \sum_i \pi_i^4 - \frac{1}{8}\alpha^2 \mathrm{i}\sum_i \left[\pi_i^2, \vec{\sigma}_i \cdot \boldsymbol{\pi}_i \times \boldsymbol{\pi}_i\right]_+ \\ & + \frac{1}{8}\alpha^2 \sum_i \left(\vec{\sigma}_i \cdot \boldsymbol{\pi}_i \times \boldsymbol{\pi}_i\right)^2, \end{aligned} \tag{7.44}$$

[3] Some text books, e.g. [66, 76], consider these terms, especially the Fermi contact interaction h^{FC}, as relativistic effects similarly with other terms that arise from the reduction from the Dirac equation to (Breit-)Pauli form, such as the Darwin term. However, according to analysis by Kutzelnigg [77], these hyperfine interactions are not relativistic effects, but may be derived also from the NR Lévy-Leblond equation.

where the anticommutator of the operators A and B is denoted as $[A,B]_+ = AB + BA$. Expanding the first term gives rise to

$$-\frac{1}{8}\alpha^2 \sum_i \pi^4 \approx h^{\mathrm{mv}} + h_{B_0}^{\mathrm{OZ-KE}} + h_K^{\mathrm{PSO-KE}} + h_L^{\mathrm{PSO-KE}} + h_{KB_0}^{\mathrm{DS-KE}} + h_{LB_0}^{\mathrm{DS-KE}} + h_{KL}^{\mathrm{DSO-KE}} + h_{KB_0}^{\mathrm{PSO-OZ}} + h_{LB_0}^{\mathrm{PSO-OZ}} + h_{KL}^{\mathrm{PSO-PSO}} + h_{B_0^2}^{\mathrm{SUSC-KE}}, \quad (7.45)$$

and the electron-spin dependent second term in Eq. (7.44) becomes

$$-\frac{1}{8}\alpha^2 \mathrm{i} \sum_i \left[\pi_i^2, \vec{\sigma}_i \cdot \boldsymbol{\pi}_i \times \boldsymbol{\pi}_i\right]_+ = -\frac{1}{8}\alpha^2 \sum_i \left[\pi_i^2, \vec{\sigma}_i \cdot \mathbf{B}_i\right]_+ \approx h_{B_0}^{\mathrm{SZ-KE}} + h_K^{\mathrm{FC-KE}} + h_L^{\mathrm{FC-KE}} + h_K^{\mathrm{SD-KE}} + h_L^{\mathrm{SD-KE}} \quad (7.46)$$

The last term to arise from $H_{\mathrm{kin}}^{\mathrm{R}}$ is

$$\frac{1}{8}\alpha^2 \sum_i \left(\vec{\sigma}_i \cdot \boldsymbol{\pi}_i \times \boldsymbol{\pi}_i\right)^2 = -\frac{1}{8}\alpha^2 \sum_i \left(\vec{\sigma}_i \cdot \mathbf{B}_i\right)^2 \approx h_{KB_0}^{\mathrm{con}} + h_{LB_0}^{\mathrm{con}} + h_{KB_0}^{\mathrm{dip}} + h_{LB_0}^{\mathrm{dip}} + h_{KL}^{\mathrm{con-dip}} + h_{KL}^{\mathrm{dip-dip}}, \quad (7.47)$$

in which the dependence on electron spin vanishes, i.e. $\left(\vec{\sigma}_i \cdot \mathbf{B}_i\right)^2 = B_i^2$, as can be seen when applying $\left(\vec{\sigma} \cdot \mathbf{A}\right)\left(\vec{\sigma} \cdot \mathbf{B}\right) = \mathbf{A} \cdot \mathbf{B} + \mathrm{i}\vec{\sigma} \cdot \mathbf{A} \times \mathbf{B}$. The corresponding "con-con" cross term, which is proportional to the product of the contact fields of two nuclei that do not coincide, vanishes everywhere in space. The one-electron SO term (7.32) divides into field-independent and -dependent SO interactions

$$\frac{1}{4}\alpha^2 \sum_K \frac{Z_K}{r_{iK}^3} \vec{\sigma}_i \cdot \left(\mathbf{r}_{iK} \times \boldsymbol{\pi}\right) \approx h^{\mathrm{SO(1)}} + h_{B_0}^{\mathrm{SO(1)}} + h_K^{\mathrm{SO(1)}} + h_L^{\mathrm{SO(1)}}. \quad (7.48)$$

Combining Eqs. (7.35) and (7.38) of the two-electron part gives rise to field-dependent and -independent two-electron spin-orbit interactions

$$-\frac{1}{4}\alpha^2 \frac{\vec{\sigma}_i \cdot \left(\mathbf{r}_{ij} \times \boldsymbol{\pi}_i\right) - \vec{\sigma}_j \cdot \left(\mathbf{r}_{ij} \times \boldsymbol{\pi}_j\right)}{r_{ij}^3} \approx h^{\mathrm{SSO(2)}} + h^{\mathrm{SOO(2)}} + h_{B_0}^{\mathrm{SSO(2)}} + h_{B_0}^{\mathrm{SOO(2)}} + h_K^{\mathrm{SSO(2)}} + h_K^{\mathrm{SOO(2)}} + h_L^{\mathrm{SSO(2)}} + h_L^{\mathrm{SOO(2)}} \quad (7.49)$$

From the first part of Eq. (7.37), two-electron counterparts of the operators in (7.42) appear, but they are neglected here. This term gives rise to the field-independent electron-electron orbital interaction term, listed e.g. in Ref. [66], and it is included in Table 7.3.2.

The terms in Tables 7.1–7.3.2 are classified according to their appearance in the orders of α, and further in accordance with their dependence on i) the electron spin, ii) the nuclear spin, and iii) the external magnetic field. Indices i, j are used to label electrons and K, L to label nuclei. The operators with dependence on the index K will appear in a similar form for nucleus L.

Table 7.1: The $\mathcal{O}(\alpha^0)$ terms of the approximate Hamiltonian, H^{BP}, in the presence of point-like nuclear magnetic dipoles and an external magnetic field.

Label	Description	Operator
h^{KE}	Kinetic energy	$-\frac{1}{2}\sum_i \nabla_i^2$
h^{NE}	Electron-nuclear Coulomb interaction	$-\sum_{i,K} \frac{Z_K}{r_{iK}}$
h^{EE}	Electron-electron Coulomb interaction	$\frac{1}{2}\sum'_{i,j} \frac{1}{r_{ij}}$
	Spin-dependence, no field-dependence	
h_K^{NQCC}	Nuclear quadrupole interaction	$-\frac{1}{2}\frac{Q_K}{I_K(2I_K-1)}\sum_i \frac{\mathbf{1}r_{iK}^2-3\mathbf{r}_{iK}\mathbf{r}_{iK}}{r_{iK}^3}$
	Field-dependence, no spin-dependence	
$h_{B_0}^{\mathrm{OZ}}$	Orbital Zeeman interaction	$\frac{1}{2}\sum_i \mathbf{l}_{iO}\cdot\mathbf{B}_0$
$h_{B_0^2}^{\mathrm{SUSC}}$	Diamagnetic susceptibility	$\frac{1}{8}\sum_i \mathbf{B}_0\cdot(\mathbf{1}r_{iO}^2-\mathbf{r}_{iO}\mathbf{r}_{iO})\cdot\mathbf{B}_0$
	Spin- and field-dependence	
$h_{B_0}^{\mathrm{SZ}}$	Electron spin Zeeman	$\frac{1}{2}g_e\sum_i \mathbf{s}_i\cdot\mathbf{B}_0$

The nuclear quadrupole interaction (NQCC) listed in Table 7.1 does not arise naturally from the present treatment, in which a point-like nucleus is assumed. It arises as the leading non-trivial term from the treatment of the Coulombic Z/r_{iK} term in presence of a finite i.e. physically correct nuclear model. However, its inclusion is necessary due to its major importance in the consideration of the spectral parameters of nuclear magnetic resonance.

The operators of H^{BP} are intuitively interpretable in terms of familiar NR concepts, and provide an interpolation step between the NR and Dirac regimes. There are inherent difficulties in Hamiltonians arising from the FW-transformation, as investigated e.g. by Moss and co-workers [78–81]. Farazdel and Smith criticised the mass-velocity term [82], pointing out that for large momenta ($p > \alpha^{-1}$), the mass-velocity term is not obtained unless the expansion of the square-root operator outside its radius of convergence is used. Most of the difficulties originate from the fact that the expansions implicitly or explicitly rely on expansion $(E-V)/2c^2$, which is invalid for particles in a Coulomb potential, where there will always be a region of space close to the nucleus in which $(E-V)/2c^2 > 1$. Furthermore, several terms pose a δ-function singularity at the origin, which is absent in the Dirac Hamiltonian. These features are ostensibly problematic, as it has been demonstrated that relativistic effects originate mostly from the region close to nucleus. Numerous quantitative studies verify, however, the practical feasibility of H^{BP} for many atomic and molecular properties.

Other difficulties arise also with regard to the self-consistent treatment of FW transformed Hamiltonians, as the eigenvalue equation $H^{\mathrm{Pauli}}\Psi = E\Psi$ yields a continuous eigenvalue spectrum without lower bound due to the mass-velocity and SO operators, unless the operator is not restricted to the solution space of the NR Hamiltonian [83].

Due to difficulties in the iterative solution of FW transformed Hamiltonians, perturbation theory has to be applied. In some cases, e.g. with the heaviest nuclei, the relativistic

Label	Description	Operator
	Scalar relativistic corrections	
h^{mv}	Mass-velocity term	$-\frac{1}{8}\alpha^2 \sum_i \nabla_i^4$
$h^{\mathrm{Dar(1)}}$	Electron-nuclear Darwin term	$\frac{\pi}{2}\alpha^2 \sum_{i,K} Z_K \delta(\mathbf{r}_{iK})$
$h^{\mathrm{Dar(2)}}$	Electron-electron Darwin term	$-\frac{\pi}{2}\alpha^2 \sum'_{i,j} \delta(\mathbf{r}_{ij})$
h^{OO}	Electron-electron orbital interaction	$\frac{1}{4}\alpha^2 \sum'_{i,j} \frac{\nabla_i \cdot \nabla_j}{r_{ij}} - \frac{(\nabla_i \cdot \mathbf{r}_{ij})(\mathbf{r}_{ij} \cdot \nabla_j)}{r_{ij}^3}$
	Spin-dependence, no field-dependence	
	Electron spin	
$h^{\mathrm{SO(1)}}$	Spin-orbit interaction	$\frac{1}{4}\alpha^2 g_e \sum_{i,K} \frac{Z_K}{r_{iK}^3} \mathbf{s}_i \cdot \mathbf{l}_{iK}$
$h^{\mathrm{SSO(2)}}$	Electron-electron spin-orbit interaction	$-\frac{1}{4}\alpha^2 g_e \sum_{i,j}{}' \mathbf{s}_i \cdot \frac{\mathbf{l}_{ij}}{r_{ij}^3}$
$h^{\mathrm{SOO(2)}}$	Electron-electron spin-other-orbit interaction	$-\frac{1}{2}\alpha^2 g_e \sum'_{i,j} \mathbf{s}_j \cdot \frac{\mathbf{l}_{ij}}{r_{ij}^3}$
$h^{\mathrm{SSD(2)}}$	Spin-spin dipolar interaction	$\frac{1}{4}\alpha^2 g_e^2 \sum'_{i,j} \frac{r_{ij}^2 (\mathbf{s}_i \cdot \mathbf{s}_j) - (\mathbf{s}_i \cdot \mathbf{r}_{ij})(\mathbf{r}_{ij} \cdot \mathbf{s}_j)}{r_{ij}^5}$
$h^{\mathrm{SSC(2)}}$	Spin-spin contact interaction	$-\frac{\pi g_e^2}{3}\alpha^2 \sum'_{i,j} \mathbf{s}_i \cdot \mathbf{s}_j \delta(\mathbf{r}_{ij})$
	Nuclear spin	
h_K^{PSO}	Orbital hyperfine interaction	$\alpha^2 \gamma_K \sum_i \mathbf{I}_K \cdot \frac{\mathbf{l}_{iK}}{r_{iK}^3}$
	Electron and nuclear spins	
h_K^{SD}	Dipolar hyperfine interaction	$\frac{1}{2}\alpha^2 g_e \gamma_K \sum_i \mathbf{s}_i \cdot \frac{3\mathbf{r}_{iK}\mathbf{r}_{iK} - \mathbf{1} r_{iK}^2}{r_{iK}^5} \cdot \mathbf{I}_K$
h_K^{FC}	Fermi contact hyperfine interaction	$\frac{4\pi}{3}\alpha^2 g_e \gamma_K \sum_i \delta(\mathbf{r}_{iK}) \mathbf{s}_i \cdot \mathbf{I}_K$

Table 7.2: Partial listing of $\mathcal{O}(\alpha^2)$ terms of the approximate Breit–Pauli Hamiltonian.

(Table 2.2 continued)

	Field-dependence, no spin-dependence	
$h_{B_0}^{\mathrm{OZ-KE}}$	Orbital Zeeman kinetic energy correction	$\frac{1}{4}\alpha^2 \sum_i \mathbf{l}_{iO} \cdot \mathbf{B}_0 \nabla_i^2$
$h_{B_0^2}^{\mathrm{SUSC-KE}}$	Diamagnetic susceptibility kinetic energy correction	$\frac{1}{32}\alpha^2 \sum_i \mathbf{B}_0 \cdot [\nabla_i^2, (\mathbf{1} r_{iO}^2 - \mathbf{r}_{iO}\mathbf{r}_{iO})]_+ \cdot \mathbf{B}_0$
	Spin- and field-dependence	
	Electron spin	
$h_{B_0}^{\mathrm{SZ-KE}}$	Electron spin Zeeman kinetic energy correction	$\frac{1}{4}\alpha^2 g_e \sum_i \mathbf{s}_i \cdot \mathbf{B}_0 \nabla_i^2$
$h_{B_0}^{\mathrm{SO(1)}}$	Spin-orbit Zeeman gauge correction	$\frac{1}{8}\alpha^2 g_e \sum_N Z_N \sum_i \mathbf{s}_i \cdot \frac{\mathbf{1}(\mathbf{r}_{iO}\cdot\mathbf{r}_{iN}) - \mathbf{r}_{iO}\mathbf{r}_{iK}}{r_{iK}^3} \cdot \mathbf{B}_0$
$h_{B_0}^{\mathrm{SSO(2)}}$	Electron-electron spin-orbit Zeeman gauge correction	$-\frac{1}{8}\alpha^2 g_e \sum'_{i,j} \mathbf{s}_i \cdot \frac{\mathbf{1}(\mathbf{r}_{iO}\cdot\mathbf{r}_{ij}) - \mathbf{r}_{iO}\mathbf{r}_{ij}}{r_{ij}^3} \cdot \mathbf{B}_0$
$h_{B_0}^{\mathrm{SOO(2)}}$	Spin-other-orbit Zeeman gauge correction	$-\frac{1}{4}\alpha^2 g_e \sum'_{i,j} \mathbf{s}_j \cdot \frac{\mathbf{1}(\mathbf{r}_{iO}\cdot\mathbf{r}_{ij}) - \mathbf{r}_{iO}\mathbf{r}_{ij}}{r_{ij}^3} \cdot \mathbf{B}_0$
	Nuclear spin	
$h_{KB_0}^{\mathrm{DS}}$	Electron nuclear Zeeman modification	$\frac{1}{2}\alpha^2 \gamma_K \sum_i \mathbf{I}_K \cdot \frac{\mathbf{1}(\mathbf{r}_{iO}\cdot\mathbf{r}_{iK}) - \mathbf{r}_{iO}\mathbf{r}_{iK}}{r_{iK}^3} \cdot \mathbf{B}_0$
$h_{KB_0}^{\mathrm{PSO-OZ}}$	Orbital hyperfine-orbital Zeeman interaction	$\frac{1}{4}\alpha^2 \gamma_K \sum_i \mathbf{I}_K \cdot \left[\frac{\mathbf{l}_{iK}}{r_{iK}^3}, \mathbf{l}_{iO}\right]_+ \cdot \mathbf{B}_0$

Label	Description	Operator
	Spin-dependence, no field-dependence	
	Nuclear spin	
$h_K^{\mathrm{PSO-KE}}$	Kinetic energy correction of the orbital hyperfine interaction	$\frac{1}{4}\alpha^4\gamma_K \sum_i \mathbf{I}_K \cdot \left[\nabla_i^2, \frac{\mathbf{l}_{iK}}{r_{iK}^3}\right]_+$
h_{KL}^{DSO}	Electron coupled nuclear spin-spin interaction	$\frac{1}{2}\alpha^4\gamma_K\gamma_L \sum_i \mathbf{I}_K \cdot \frac{\mathbf{1}(\mathbf{r}_{iK}\cdot\mathbf{r}_{iL})-\mathbf{r}_{iK}\mathbf{r}_{iL}}{r_{iK}^3 r_{iL}^3} \cdot \mathbf{I}_L$
$h_{KL}^{\mathrm{DSO-KE}}$	Kinetic energy correction of the electron coupled nuclear spin-spin interaction	$\frac{1}{8}\alpha^6\gamma_K\gamma_L \sum_i \mathbf{I}_K \cdot \left[\nabla_i^2, \frac{\mathbf{1}(\mathbf{r}_{iK}\cdot\mathbf{r}_{iL})-\mathbf{r}_{iK}\mathbf{r}_{iL}}{r_{iK}^3 r_{iL}^3}\right]_+ \cdot \mathbf{I}_L$
$h_{KL}^{\mathrm{PSO-PSO}}$	Orbital hyperfine coupled nuclear spin-spin interaction	$\frac{1}{2}\alpha^6\gamma_K\gamma_L \sum_i \mathbf{I}_K \cdot \left[\frac{\mathbf{l}_{iK}}{r_{iK}^3}, \frac{\mathbf{l}_{iL}}{r_{iL}^3}\right]_+ \cdot \mathbf{I}_L$
$h_{KL}^{\mathrm{con-dip}}$	Contact hyperfine coupled nuclear spin-spin interaction	$-\frac{2\pi}{3}\alpha^6\gamma_K\gamma_L \sum_i \mathbf{I}_K \cdot \left[\delta(\mathbf{r}_{iK})\frac{3\mathbf{r}_{iL}\mathbf{r}_{iL}-\mathbf{1}r_{iL}^2}{r_{iL}^5} + \delta(\mathbf{r}_{iL})\frac{3\mathbf{r}_{iK}\mathbf{r}_{iK}-\mathbf{1}r_{iK}^2}{r_{iK}^5}\right] \cdot \mathbf{I}_L$
$h_{KL}^{\mathrm{dip-dip}}$	Dipolar hyperfine coupled nuclear spin-spin interaction	$-\frac{1}{4}\alpha^6\gamma_K\gamma_L \sum_i \mathbf{I}_K \cdot \frac{1}{r_{iK}^5 r_{iK}^5}[9\mathbf{r}_{iK}\mathbf{r}_{iL}(\mathbf{r}_{iK}\cdot\mathbf{r}_{iL}) - 3\mathbf{r}_{iK}\mathbf{r}_{iL}(r_{iK}^2 + r_{iL}^2)$ $+\mathbf{1}(r_{iK}^2 r_{iL}^2)] \cdot \mathbf{I}_L$
	Electron and nuclear spins	
$h_K^{\mathrm{SD-KE}}$	Kinetic energy correction of the dipolar hyperfine interaction	$\frac{1}{8}\alpha^4 g_e\gamma_K \sum_i \mathbf{s}_i \cdot \left[\nabla_i^2, \frac{3\mathbf{r}_{iK}\mathbf{r}_{iK}-\mathbf{1}r_{iK}^2}{r_{iK}^5}\right]_+ \cdot \mathbf{I}_K$
$h_K^{\mathrm{FC-KE}}$	Kinetic energy correction of the Fermi contact interaction	$\frac{\pi}{3}\alpha^4 g_e\gamma_K \sum_i \mathbf{s}_i \cdot [\nabla_i^2, \delta(\mathbf{r}_{iK})]_+ \cdot \mathbf{I}_K$
$h_K^{\mathrm{SO(1)}}$	Spin-orbit hyperfine correction	$\frac{1}{4}\alpha^4 g_e\gamma_K \sum_N Z_N \sum_i \mathbf{s}_i \cdot \frac{\mathbf{1}(\mathbf{r}_{iK}\cdot\mathbf{r}_{iN})-\mathbf{r}_{iK}\mathbf{r}_{iN}}{r_{iK}^3 r_{iN}^3} \cdot \mathbf{I}_K$
$h_K^{\mathrm{SSO(2)}}$	Spin-same-orbit hyperfine correction	$-\frac{1}{4}\alpha^4 g_e\gamma_K \sum'_{i,j} \mathbf{s}_i \cdot \frac{\mathbf{1}(\mathbf{r}_{iK}\cdot\mathbf{r}_{ij})-\mathbf{r}_{iK}\mathbf{r}_{ij}}{r_{iK}^3 r_{ij}^3} \cdot \mathbf{I}_K$
$h_K^{\mathrm{SOO(2)}}$	Spin-other-orbit hyperfine correction	$-\frac{1}{2}\alpha^4 g_e\gamma_K \sum'_{i,j} \mathbf{s}_j \cdot \frac{\mathbf{1}(\mathbf{r}_{iK}\cdot\mathbf{r}_{ij})-\mathbf{r}_{iK}\mathbf{r}_{ij}}{r_{iK}^3 r_{ij}^3} \cdot \mathbf{I}_K$
	Spin- and field-dependence	
	Nuclear spin	
$h_{KB_0}^{\mathrm{DS-KE}}$	Kinetic energy correction of the electron nuclear Zeeman modification	$\frac{1}{8}\alpha^4\gamma_K \sum_i \mathbf{I}_K \cdot \left[\nabla_i^2, \frac{\mathbf{1}(\mathbf{r}_{iO}\cdot\mathbf{r}_{iK})-\mathbf{r}_{iO}\mathbf{r}_{iK}}{r_{iK}^3}\right]_+ \cdot \mathbf{B}_0$
$h_{KB_0}^{\mathrm{con}}$	Nuclear spin Zeeman contact hyperfine interaction	$-\frac{2\pi}{3}\alpha^4\gamma_K \sum_i \delta(\mathbf{r}_{iK})\mathbf{I}_K \cdot \mathbf{B}_0$
$h_{KB_0}^{\mathrm{dip}}$	Nuclear spin Zeeman dipolar hyperfine interaction	$-\frac{1}{4}\alpha^4\gamma_K \sum_i \mathbf{I}_K \cdot \frac{3\mathbf{r}_{iK}\mathbf{r}_{iK}-\mathbf{1}r_{iK}^2}{r_{iK}^5} \cdot \mathbf{B}_0$

Table 7.3: Partial listing of $\mathcal{O}(\alpha^4)$ and $\mathcal{O}(\alpha^6)$ terms of the approximate Hamiltonian.

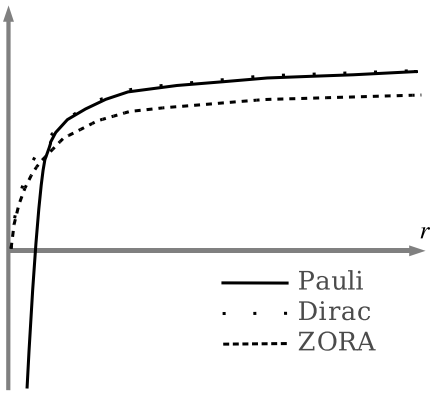


Figure 7.1: A schematic illustration of the behaviour of ZORA and Pauli approximations with respect to the Dirac equation. Drawn after Ref. [74].

effects may be so large that a perturbation theoretical approach is inadequate.

7.3.3 Other quasi-relativistic Hamiltonians

As discussed above, there are difficulties in two-component transformations of the Dirac Hamiltonian, which arise in the form of divergent terms and singularities when $r \to 0$.

An alternative approach for decoupling the large and small components of the Dirac equation is the zeroth-order regular approximation (ZORA) Hamiltonian [84]. The derivation of the ZORA Hamiltonian proceeds almost in complete analogy with that of the Pauli Hamiltonian, except here the expansion is carried out with respect to $E/(2c^2 - V)$. In the derivation of the ZORA Hamiltonian, one proceeds almost in complete analogy with Pauli Hamiltonian, but the expansion is carried out with respect to $E/(2c^2 - V)$. The Hamiltonian becomes

$$H^{\mathrm{ZORA}} = V + \frac{1}{2}\mathbf{p}\mathcal{K}\mathbf{p} + \frac{i}{2}\sigma((\mathbf{p}\mathcal{K}) \times \mathbf{p}), \tag{7.50}$$

where $\mathcal{K} = (1 - \frac{1}{2}\alpha^2 V)^{-1}$. It has similarities with the earlier Chang-Pelisser-Durand zeroth-order effective Hamiltonian [85]. It has been shown that ZORA behaves well near to nucleus, and that it is variationally stable at zeroth-order. ZORA contains similar relativistic corrections as are present in the Pauli Hamiltonian but in a regularised form. The inclusion of the first-order in the expansion yields FORA (first-order regular approximation). ZORA is bounded from below, up to $Z = 137$. It has the flaws of not being gauge invariant, and the ignoring the change in the metrics is problematic. The features and differences between the Pauli and ZORA approximations are outlined in Figure 7.1, in which the x-axis is the distance r from the nucleus.

The Pauli approximation breaks down near the nucleus but approaches the correct limit at large r. ZORA is bounded from below, up to $Z = 137$, and it is a good approximation for $|V| \gg |E| > 0$, i.e. where the potential dominates, but it does behave erroneously when

energies and distances are large [74,86]. for large energies and large distances from nucleus ZORA possesses a dependence on the choice of the zero of the potential, nd in it only the eigenvalue spectrum, not the eigenfunctions, reflect the actual physics. This is often referred to as the picture change effect. This difference is due to the fact that the change of picture [87] is neglected and that the ZORA Hamiltonian does not contain all terms of the α^2 order.

The scaled ZORA includes the change in metric, but the picture change is still ignored. There are other ideas for the regular approximation scheme. In exponential regular approximation (ERA) [88], an exponential function is added to the definition of the small component in order to correct the metrics. The idea is to remove the singularity as with ZORA, without introducing the long-range dependence into the ansatz. In modified ERA (MERA) [88], part of the relativistic contribution is omitted to avoid spin-orbit terms in the metric. In infinite-order regular approximation (IORA) [89, 90] and its MERA-type modification (MIORA) [88], the expansion may be taken to infinite order by using an unnormalised FW transformation, which results in the ZORA Hamiltonian and a non-unit metric. Filatov and Cremer [91] presented a scaled IORA (SIORA) method, in which an effective energy-independent relativistic Hamiltonian was obtained by a regular expansion of the exact Hamiltonian for electronic states in terms of linear energy-independent operators.

Another alternative is an approach with external field projectors. This method has been developed by Hess [92,93] on the basis of theoretical work by Sucher [94] and Douglas and Kroll [95]. This scheme is often called the Douglas-Kroll-Hess (DKH) method. In the method, the FW transformation is carried out up to the first order in the momentum space, and the result is then split into odd and even parts. After that, the FW transformation is repeated to order n, with antihermitian matrices W_n, $U_n = \sqrt{1 + W_n^2} + W_n$. The form of the W's is chosen to cancel certain terms. The resulting Hamiltonian is decoupled, i.e. it operates on the large and small components independently, to order $n + 1$. Already U_1 includes several relativistic phenomena. DKH is widely used in molecular calculations. It has the benefit of being bounded from below, with no unphysical states occuring. It also approaches the correct NR limit.

Several quasi-relativistic schemes based on the elimination of the small component or other approach have been presented in Refs. [96–102].

Yet another alternative is to apply perturbation theory straight to the Dirac equation, and to change the metrics between the large and small component, yielding direct (or Dirac) perturbation theory (DPT) [103–105]. This approach gives non-singular forms for energy and wave function to arbitrary order. However, it is computationally almost as expensive as using the four-component framework, and its implementation is considered to be difficult.

Besides in the Hamiltonian, the relativistic effects can partly be included as "artifacts" in the formally non-relativistic calculations themselves by using the relativistic effective core potential (ECP) approach (see e.g. Refs. [106] or [107] and references therein).

Appendix A

Second quantization

A.1 Basic concepts

In the standard formulation of quantum mechanics (such as that employed in the previous chapters) observables are represented by operators and states as functions. In second quantization (SQ) formalism [108], also the wave functions are represented in terms of operators.

A.1.1 Occupation number vectors

In the SQ formalism, each Slater determinant (1.27) of M orthonormal spin-orbitals is represented by an *occupation number vector* (ON) $\mathbf{k}$,

$$|\mathbf{k}\rangle = |k_1,\, k_2,\, \ldots, k_M\rangle\,, \qquad k_P = \begin{cases} 1 & \psi_P \text{ occupied} \\ 0 & \psi_P \text{ unoccupied} \end{cases} \tag{A.1}$$

in an abstract vector space called the *Fock space*.

For an orthonormal set of spin-orbitals, we define the *inner product* between two ON vectors as

$$\langle \mathbf{m} \,|\mathbf{k}\rangle = \prod_{P=1}^{M} \delta_{m_P k_P}. \tag{A.2}$$

This definition is consistent with the overlap between two Slater determinants, but has a well-defined but zero overlap between states with *different electron numbers* is a special feature of the Fock-space formulation. It allows for a unified description of systems with variable numbers of electrons.

- In a given spin-orbital basis, there is a one-to-one mapping between the Slater determinants with spin-orbitals in a canonical order and the ON vectors in the Fock space.
- However, ON vectors are *not* Slater determinants: ON vectors have no spatial structure but are just basis vectors in an abstract vector space.

- The Fock space can be manipulated as an ordinary inner-product vector space.

The ON vectors constitute an orthonormal basis in the 2^M dimensional Fock space $F(M)$, that can be decomposed as a direct sum of subspaces,

$$F(M) = F(M,0) \oplus F(M,1) \oplus \cdots \oplus F(M,N), \tag{A.3}$$

where $F(M,N)$ contains all ON vectors obtained by distributing N electrons among the M spin-orbitals, in other words, all ON vectors for which the sum of occupation number is N. The subspace $F(M,0)$ is the *vacuum state*,

$$|\text{vac}\rangle = |0_1,\, 0_2, \ldots,\, 0_M\rangle\,. \tag{A.4}$$

Approximations to an exact N-electron wave function are expressed in terms of vectors in the Fock subspace $F(M,N)$ of dimension equal to $\binom{M}{N}$.

A.1.2 Creation and annihilation operators

In second quantization, all operators and states can be constructed from a set of elementary *creation* and *annihilation* operators. The M creation operators are defined by

$$\begin{aligned} a_P^\dagger\,|k_1,\, k_2, \ldots,\, 0_P, \ldots,\, k_M\rangle &= \Gamma_P^{\mathbf{k}}\,|k_1,\, k_2, \ldots,\, 1_P, \ldots,\, k_M\rangle & \text{(A.5)}\\ a_P^\dagger\,|k_1,\, k_2, \ldots,\, 1_P, \ldots,\, k_M\rangle &= 0 & \text{(A.6)} \end{aligned}$$

where

$$\Gamma_P^{\mathbf{k}} = \prod_{Q=1}^{P-1} (-1)^{k_Q}. \tag{A.7}$$

The definition can be also combined a single equation:

$$a_P^\dagger\,|k_1,\, k_2, \ldots,\, 0_P, \ldots,\, k_M\rangle = \delta_{k_P 0}\Gamma_P^{\mathbf{k}}\,|k_1,\, k_2, \ldots,\, 1_P, \ldots,\, k_M\rangle \tag{A.8}$$

Operating twice with $a_P^\dagger$ on an ON vector gives

$$a_P^\dagger a_P^\dagger\,|k_1,\, k_2, \ldots,\, 0_P, \ldots,\, k_M\rangle = a_P^\dagger \delta_{k_P 0}\Gamma_P^{\mathbf{k}}\,|k_1,\, k_2, \ldots,\, 1_P, \ldots,\, k_M\rangle = 0,$$

therefore

$$a_P^\dagger a_P^\dagger = 0. \tag{A.9}$$

For $Q > P$,

$$\begin{aligned} a_P^\dagger a_Q^\dagger\,|\ldots,\, k_P, \ldots,\, k_Q, \ldots\rangle &= a_P^\dagger \delta_{k_Q 0}\Gamma_Q^{\mathbf{k}}\,|\ldots,\, k_P, \ldots,\, 1_Q, \ldots\rangle \\ &= \delta_{k_P 0}\delta_{k_Q 0}\Gamma_P^{\mathbf{k}}\Gamma_Q^{\mathbf{k}}\,|\ldots,\, 1_P, \ldots,\, 1_Q, \ldots\rangle\,. \end{aligned}$$

Reversing the order of the operators,

$$\begin{aligned} a_Q^\dagger a_P^\dagger \left|\ldots,\, k_P, \ldots,\, k_Q, \ldots\right\rangle &= a_Q^\dagger \delta_{k_P 0} \Gamma_P^{\mathbf{k}} \left|\ldots,\, 1_P, \ldots,\, k_Q, \ldots\right\rangle \\ &= \delta_{k_P 0}\delta_{k_Q 0} \Gamma_P^{\mathbf{k}} (-\Gamma_Q^{\mathbf{k}}) \left|\ldots,\, 1_P, \ldots,\, 1_Q, \ldots\right\rangle . \end{aligned}$$

and combining the results, we obtain

$$a_P^\dagger a_Q^\dagger + a_Q^\dagger a_P^\dagger \left|\mathbf{k}\right\rangle = 0.$$

Substitution of dummy indices shows that this holds for $Q < P$ as well, and is true also for $Q = P$. Since $\left|\mathbf{k}\right\rangle$ is an arbitrary ON vector, we conclude the anticommutation relation

$$a_P^\dagger a_Q^\dagger + a_Q^\dagger a_P^\dagger = [a_P^\dagger, a_Q^\dagger]_+ = 0. \tag{A.10}$$

The properties of the *adjoint* or conjugate operators a_P can be reasoned from those of the creation operators. Thus, the adjoint operators satisfy the anticommutation relation

$$[a_P, a_Q]_+ = 0. \tag{A.11}$$

Let us invoke the *resolution of the identity*:

$$a_P \left|\mathbf{k}\right\rangle = \sum_{\mathbf{m}} \left|\mathbf{m}\right\rangle \left\langle \mathbf{m}\right| a_P \left|\mathbf{k}\right\rangle ,$$

where, using Eq. (A.8),

$$\left\langle \mathbf{m}\right| a_P \left|\mathbf{k}\right\rangle = \left\langle \mathbf{k}\right| a_P \left|\mathbf{m}\right\rangle^* = \begin{cases} \delta_{m_P 0} \Gamma_P^{\mathbf{m}} & \text{if } k_Q = m_Q + \delta_{QP} \\ 0 & \text{otherwise} \end{cases} .$$

From the definition of Γ and from $k_Q = m_Q + \delta_{QP}$ we see that $\Gamma_P^{\mathrm{m}} = \Gamma_P^{\mathrm{K}}$. We may therefore write the equation as

$$\left\langle \mathbf{m}\right| a_P \left|\mathbf{k}\right\rangle = \begin{cases} \delta_{k_P 1} \Gamma_P^{\mathbf{k}} & \text{if } m_Q = k_Q - \delta_{QP} \\ 0 & \text{otherwise} \end{cases} .$$

Hence, only one term in $a_P \left|\mathbf{k}\right\rangle$ survives:

$$a_P \left|\mathbf{k}\right\rangle = \delta_{k_P 1} \Gamma_P^{\mathbf{k}} \left|k_1, \ldots, 0_P, \ldots, k_M\right\rangle . \tag{A.12}$$

The operator a_P is called the *annihilation operator*.

Combining Eqs. (A.8) and (A.12), we get

$$a_P^\dagger a_P \left|\mathbf{k}\right\rangle = \delta_{k_P 1} \left|\mathbf{k}\right\rangle \tag{A.13}$$

$$a_P a_P^\dagger \left|\mathbf{k}\right\rangle = \delta_{k_P 0} \left|\mathbf{k}\right\rangle \tag{A.14}$$

that leads to

$$a_P^\dagger a_P + a_P a_P^\dagger = 1. \tag{A.15}$$

For $P > Q$, we have

$$\begin{aligned} a_P^\dagger a_Q \left|\mathbf{k}\right\rangle &= -\delta_{k_P 0}\delta_{k_Q 1}\Gamma_P^{\mathbf{k}}\Gamma_Q^{\mathbf{k}} \left|k_1, \ldots, 0_Q, \ldots, 1_P, \ldots, k_M\right\rangle \\ a_Q a_P^\dagger \left|\mathbf{k}\right\rangle &= \delta_{k_P 0}\delta_{k_Q 1}\Gamma_P^{\mathbf{k}}\Gamma_Q^{\mathbf{k}} \left|k_1, \ldots, 0_Q, \ldots, 1_P, \ldots, k_M\right\rangle, \end{aligned}$$

thus we have the operator identity

$$a_P^\dagger a_Q + a_Q a_P^\dagger = 0 \qquad P > Q. \tag{A.16}$$

Hence,

$$a_P^\dagger a_Q + a_Q a_P^\dagger = [a_P^\dagger, a_Q]_+ = \delta_{PQ}. \tag{A.17}$$

A.1.3 Number-conserving operators

The *occupation-number operator* that counts the number of electrons in spin-orbital P is introduced as

$$\hat{N}_P = a_P^\dagger a_P, \qquad \hat{N}_P \left|\mathbf{k}\right\rangle = k_P \left|\mathbf{k}\right\rangle \tag{A.18}$$

The occupation-number operators are Hermitian, $\hat{N}^\dagger = \hat{N}$, as well as idempotent, $\hat{N}_P^2 = \hat{N}_P$. Using the basic anticommutation relations, we obtain

$$[\hat{N}_P, a_Q^\dagger] = \delta_{PQ} a_Q^\dagger \tag{A.19}$$

$$\left[\hat{N}_P, a_Q\right] = -\delta_{PQ} a_Q \tag{A.20}$$

So for an arbitrary string $\hat{X}$ consisting of creation and annihilation operators, e.g. $\hat{X} = a_P^\dagger a_Q a_P a_R^\dagger a_S$, the commutators with $\hat{N}$ become

$$[\hat{N}_P, \hat{X}] = N_P^X \hat{X}, \tag{A.21}$$

where N_P^X is the number of times $a_P^\dagger$ occurs in $\hat{X}$ minus the number of times a_P occurs.

All occupation-number operators added together in the Fock space gives the Hermitian operator

$$\hat{N} = \sum_{P=1}^{M} a_P^\dagger a_P, \tag{A.22}$$

which returns the *number of electrons in an ON vector*, $\hat{N}\left|\mathbf{k}\right\rangle = N\left|\mathbf{k}\right\rangle$, and is therefore known as the *particle-number operator*. We find that the number operator commutes with any string $\hat{T}$ that contains an equal number of creation and annihilation operators. Such strings are called *number-conserving*. In general, the application of the string $\hat{X}$ to a Fock-space vector increases the number of electrons by N^X.

The simplest number-conserving operators are the elementary *excitation operators*

$$\hat{E}_Q^P = a_P^\dagger a_Q, \tag{A.23}$$

which give as applied to an ON vector

$$\begin{aligned} a_P^\dagger a_Q \left|\mathbf{k}\right\rangle &= a_P^\dagger \delta_{k_Q 1} \Gamma_Q^{\mathbf{k}} \left|k_1, \ldots, 0_Q, \ldots, k_P, \ldots, k_M\right\rangle \\ &= \delta_{k_P 0} \delta_{k_Q 1} \Gamma_Q^{\mathbf{k}} \Gamma_P^{\mathbf{k}} \varepsilon_{PQ} \left|k_1, \ldots, 0_Q, \ldots, 1_P, \ldots, k_M\right\rangle \\ &= \varepsilon_{PQ} \Gamma_Q^{\mathbf{k}} \Gamma_P^{\mathbf{k}} (1 - k_P) k_Q \left| \begin{matrix} k_P \to 1 \\ k_Q \to 0 \end{matrix} \right\rangle \end{aligned} \tag{A.24}$$

where

$$\varepsilon_{PQ} = \begin{cases} 1 & P \leq Q \\ -1 & P > Q \end{cases}.$$

The case $P < Q$ differs from this result only in the interpretation of ε_{PQ}, whereas the case $P = Q$ is covered by Eq. (A.18). Therefore we may write

$$a_P^\dagger a_Q \left|\mathbf{k}\right\rangle = \varepsilon_{PQ} \Gamma_P^{\mathbf{k}} \Gamma_Q^{\mathbf{k}} (1 - k_P + \delta_{PQ}) k_Q \left| \begin{matrix} k_P \to 1 \\ k_Q \to \delta_{PQ} \end{matrix} \right\rangle. \tag{A.25}$$

The application of a single such operator gives a single excitation, two a double excitation and so forth.

A.2 The representation of one- and two-electron operators

Expectation values of Hermitian operators correspond to physical observables and should thus be independent of the representation of operators and states. Therefore, we require the matrix element of a second-quantization operator between two ON vectors to be equal to its first-quantization counterpart.

To determine the numerical parameters f_{PQ} in the second-quantization representation of one-electron operators, we evaluate the matrix elements of $\hat{f}$ between two ON vectors and compare with the usual Slater rules for matrix elements between determinants. We are lead to the identification

$$f_{PQ} = \left\langle \psi_P \left| \hat{f}^c \right| \psi_Q \right\rangle \tag{A.26}$$

$$g_{PQRS} = \left\langle \psi_P \psi_R \left| \hat{g}^c \right| \psi_Q \psi_S \right\rangle. \tag{A.27}$$

The parameters g_{PQRS} possess the particle-interchange symmetry,

$$g_{PQRS} = g_{RSPQ}. \tag{A.28}$$

In the case of real spin-orbitals, the integrals exhibit the following permutational symmetries:

$$f_{PQ} = f_{QP} \tag{A.29}$$

$$g_{PQRS} = g_{QPRS} = g_{PQSR} = g_{QPSR}, \tag{A.30}$$

of which the latter may be further combined with Eq. (A.28) to yield an eight-fold symmetry.

Using the introduced second-quantization representation, we may now construct the (non-relativistic, spin-free) molecular electronic Hamiltonian in the Born–Oppenheimer approximation,

$$\hat{H} = \sum_{PQ} h_{PQ} a_P^\dagger a_Q + \frac{1}{2} g_{PQRS} a_P^\dagger a_R^\dagger a_S a_Q + h_{\text{nuc}}, \tag{A.31}$$

where

$$h_{PQ} = \int \psi_P^*(\mathbf{x}) \left(-\frac{1}{2}\nabla^2 - \sum_I \frac{Z_I}{r_{iI}} \right) \psi_Q(\mathbf{x}) d\mathbf{x} \tag{A.32}$$

$$g_{PQRS} = \int \frac{\psi_P^*(\mathbf{x})\psi_R^*(\mathbf{x})\psi_Q(\mathbf{x})\psi_S(\mathbf{x})}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2 \tag{A.33}$$

$$h_{\text{nuc}} = \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{R_{IJ}}. \tag{A.34}$$

The form of the second-quantization Hamiltonian can be interpreted in the following way: Applied to an electronic state, the Hamiltonian produces a linear combination of the original state with states generated by single and double electron excitations from this state. With each such excitation, there is an associated *amplitude* h_{PQ} or g_{PQRS}, which represents the probability of this event happening.

Let $\hat{A}^c$, $\hat{B}^c$ and $\hat{C}^c$ be one-electron operators in first quantization and $\hat{A}$, $\hat{B}$ and $\hat{C}$ be the corresponding second-quantization representations.

- The first-quantization operator $a\hat{A}^c + b\hat{B}^c$, where a and b are numbers, is represented by $a\hat{A} + b\hat{B}$.

- The standard relations

$$\hat{A}(\hat{B}\hat{C}) = (\hat{A}\hat{B})\hat{C} \tag{A.35}$$

$$(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger \tag{A.36}$$

  are valid.

- For a *complete* one-electron basis

$$\hat{C}^c = \hat{A}^c \hat{B}^c \Rightarrow \hat{C} = \hat{A}\hat{B}$$

  but for *finite* basis sets this expression does not hold. The second-quantization operators are projections of the exact operators onto a basis of spin-orbitals. For an incomplete basis, the second-quantization representation of an operator product depends on when the projection is made.

First quantization	Second quantization
• One-electron operator: $$\hat{f}^c = \sum_{i=1}^{N} f(\mathbf{x}_i)$$	• One-electron operator: $$\hat{f} = \sum_{PQ} f_{PQ} a_P^\dagger a_Q$$
• Two-electron operator: $$\hat{g}^c = \sum_{i=1}^{N} \sum_{j=i+1}^{N} g(\mathbf{x}_i, \mathbf{x}_j)$$	• Two-electron operator: $$\hat{g} = \frac{1}{2} \sum_{PQRS} g_{PQRS} a_P^\dagger a_R^\dagger a_S a_Q$$
• Operators are independent of the spin-orbital basis	• Operators depend on the spin-orbital basis
• Operators depend on the number of electrons	• Operators are independent of electrons
• Operators are exact	• Projected operators

Table A.1: Comparison between first and second quantization representations.

Second quantization treats operators and wave functions in a unified way – they are all expressed in terms of the elementary creation and annihilation operators: any ON vector may be written as

$$|\mathbf{k}\rangle = \hat{X}_{\mathbf{k}} |\text{vac}\rangle = \left[\prod_{P=1}^{M} (a_P^\dagger)^{k_P} \right] |\text{vac}\rangle \tag{A.37}$$

and therefore the matrix elements can be viewed as the *vacuum expectation value* of an operator

$$\left\langle \mathbf{k} \middle| \hat{O} \middle| \mathbf{m} \right\rangle = \left\langle \text{vac} \middle| \hat{X}_{\mathbf{k}}^\dagger \hat{O} \hat{X}_{\mathbf{m}} \middle| \text{vac} \right\rangle, \tag{A.38}$$

and expectation values become linear combinations of vacuum expectation values.

A.3 Commutators and anticommutators

In the manipulation of operators and matrix elements in second quantization, the commutator $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$ and the anticommutator $[\hat{A}, \hat{B}]_+ = \hat{A}\hat{B} + \hat{B}\hat{A}$ of two operators are often encountered. Referring to the basic relations of the elementary creation and annihilation operators, it is usually possible to simplify the commutators and anticommutators between strings of elementary operators considerably.

We need to introduce the concepts of operator *rank* and rank reduction.

- The (particle) rank of a string of creation and annihilation operators is simply *the number of elementary operators divided by 2.*

- Rank reduction is said to occur when the rank of a commutator or anticommutator is lower than the combined rank of the operators commuted or anticommuted.

A simple rule

- Rank reduction follows upon anticommutation of two strings of half-integral rank and upon commutation of all other strings

is useful for simplifying the expressions.

One useful strategy for the evaluation of commutators and anticommutators is based on their linear expansion in simpler commutators or anticommutators according to e.g. the following operator identities, and aim at greatest possible rank reduction:

$$\left[\hat{A}, \hat{B}_1\hat{B}_2\right] = [\hat{A}, \hat{B}_1]\hat{B}_2 + \hat{B}_1[\hat{A}, \hat{B}_2] \tag{A.39}$$

$$\left[\hat{A}, \hat{B}_1\cdots\hat{B}_n\right] = \sum_{k=1}^{n} \hat{B}_1\cdots\hat{B}_{k-1}[\hat{A}, \hat{B}_k]\hat{B}_{k+1}\cdots\hat{B}_n \tag{A.40}$$

$$\left[\hat{A}, \hat{B}_1\hat{B}_2\right] = [\hat{A}, \hat{B}_1]_+\hat{B}_2 - \hat{B}_1[\hat{A}, \hat{B}_2]_+ \tag{A.41}$$

$$\left[\hat{A}, \hat{B}_1\cdots\hat{B}_n\right] = \sum_{k=1}^{n}(-1)^{k-1}\hat{B}_1\cdots[\hat{A}, \hat{B}_k]_+\cdots\hat{B}_n \ (n\,\text{even}) \tag{A.42}$$

$$\left[\hat{A}, \hat{B}_1\hat{B}_2\right]_+ = [\hat{A}, \hat{B}_1]\hat{B}_2 + \hat{B}_1[\hat{A}, \hat{B}_2]_+ = [\hat{A}, \hat{B}_1]_+\hat{B}_2 - \hat{B}_1[\hat{A}, \hat{B}_2] \tag{A.43}$$

$$\left[\hat{A}, \hat{B}_1\cdots\hat{B}_n\right]_+ = \sum_{k=1}^{n}(-1)^{k-1}\hat{B}_1\cdots[\hat{A}, \hat{B}_k]_+\cdots\hat{B}_n \ (n\,\text{odd}). \tag{A.44}$$

Let us consider the simplest nontrivial commutator, $[a_P^\dagger, a_Q^\dagger a_R]$. Moving one of the operators after the comma out of the commutators by using (A.41),

$$[a_P^\dagger, a_Q^\dagger a_R] = [a_P^\dagger, a_Q^\dagger]_+ a_R - a_Q^\dagger[a_P^\dagger, a_R]_+ \tag{A.45}$$

and invoking the basic anticommutation relation we have

$$[a_P^\dagger, a_Q^\dagger a_R] = -\delta_{PR}a_Q^\dagger. \tag{A.46}$$

Similarly,

$$[a_P, a_Q^\dagger a_R] = \delta_{PQ}a_R. \tag{A.47}$$

Then, let us evaluate the commutator between two excitation operators, using the results from the previous example,

$$[a_P^\dagger a_Q, a_R^\dagger a_S] = [a_P^\dagger, a_R^\dagger a_S^\dagger]a_R + a_P^\dagger[a_Q, a_R^\dagger a_S] = \delta_{QR}a_P^\dagger a_S - \delta_{PS}a_R^\dagger a_Q. \tag{A.48}$$

A slightly more complicated commutator is evaluated by applying Eq. (A.39) and the previous result:

$$\begin{aligned}[a_P^\dagger a_Q, a_R^\dagger a_S a_M^\dagger a_N] &= [a_P^\dagger a_Q, a_R^\dagger a_S] a_M^\dagger a_N + a_R^\dagger a_S [a_P^\dagger a_Q, a_M^\dagger a_N] \\ &= \delta_{QR} a_P^\dagger a_S a_M^\dagger a_N - \delta_{PS} a_R^\dagger a_Q a_M^\dagger a_N \\ &\quad + \delta_{QM} a_R^\dagger a_S a_P^\dagger a_N - \delta_{PN} a_R^\dagger a_S a_M^\dagger a_Q. \end{aligned} \tag{A.49}$$

The following *double commutator* can be evaluated by invoking the result (A.48) twice

$$\begin{aligned}[a_P^\dagger a_Q, [a_R^\dagger a_S, a_M^\dagger a_N]] &= \delta_{SM} [a_P^\dagger a_Q, a_R^\dagger a_N^\dagger] - \delta_{RN} [a_P^\dagger a_Q, a_M^\dagger a_S] \\ &= \delta_{SM}\delta_{QR} a_P^\dagger a_N - \delta_{SM}\delta_{PM} a_R^\dagger a_Q - \delta_{RN}\delta_{QM} a_P^\dagger a_S \\ &\quad + \delta_{RN}\delta_{PS} a_M^\dagger a_Q. \end{aligned} \tag{A.50}$$

This gives rise to a rank reduction by 2.

A.4 Orbital rotations

In many situations, e.g., during the optimization of an approximate electronic state or in the calculation of the response of an electronic state to an external perturbation, it becomes necessary to carry out transformations between different sets of orthonormal spin-orbitals.

We shall encounter especially cases where the occupation numbers refer to a set of orthonormal spin-orbitals $\tilde{\psi}_P$ that is obtained from another set ψ_P by a *unitary transformation*

$$\tilde{\psi}_P = \sum_Q \psi_Q U_{QP}. \tag{A.51}$$

Here, a *unitary matrix* $\mathbf{U}$ is a matrix that fulfills the relation

$$\mathbf{U}^\dagger \mathbf{U} = \mathbf{U}\mathbf{U}^\dagger = \mathbf{1}. \tag{A.52}$$

The *spectral theorem* states that any unitary matrix can be diagonalized as

$$\mathbf{U} = \mathbf{V}\boldsymbol{\epsilon}\mathbf{V}^\dagger,$$

where $\mathbf{V}$ is unitary and $\boldsymbol{\epsilon}$ a complex diagonal matrix, $\epsilon_{kk} = \exp(i\delta_k)$. Therefore any unitary matrix can be written as the matrix exponential[1] of an anti-Hermitian matrix:

$$\begin{aligned}\mathbf{U} &= \mathbf{V}\exp(i\boldsymbol{\delta})\mathbf{V}^\dagger = \exp(i\mathbf{V}\boldsymbol{\delta}\mathbf{V}^\dagger) \\ &\equiv \exp(\mathbf{X}), \qquad \mathbf{X} = -\mathbf{X}^\dagger. \end{aligned} \tag{A.53}$$

By an introduction of the anti-Hermitian operator

$$\hat{\kappa} = \sum_{PQ} \kappa_{PQ} a_P^\dagger a_Q, \qquad \hat{\kappa}^\dagger = -\hat{\kappa}, \tag{A.54}$$

[1]The matrix exponential is defined as $\exp(\mathbf{A}) = \sum_{n=0}^{\infty} \mathbf{A}^n/n!$.

where the parameters κ_{PQ} are the elements of an anti-Hermitian matrix $\boldsymbol{\kappa}$, for which $\mathbf{U} = \exp(-\boldsymbol{\kappa})$, the elementary operators $\tilde{a}_P^\dagger$, $\tilde{a}_P$ and state $\left|\tilde{0}\right\rangle$ generated by the unitary transformation (A.51) can be expressed in terms of the untransformed operators and states as

$$\begin{aligned} \tilde{a}_P^\dagger &= \exp(-\hat{\kappa}) a_P^\dagger \exp(\hat{\kappa}) && \text{(A.55)} \\ \tilde{a}_P &= \exp(-\hat{\kappa}) a_P \exp(\hat{\kappa}) && \text{(A.56)} \\ \left|\tilde{0}\right\rangle &= \exp(-\hat{\kappa}) \left|0\right\rangle . && \text{(A.57)} \end{aligned}$$

A.5 Spin in second quantization

In the formalism of second quantization, there is no reference to electron spin. However, in non-relativistic theory, many important simplifications follow by taking spin explicitly into account.

A.5.1 Notation

We shall separate the orbital space and the spin space,[2] that is, a spin orbital will be denoted by $\psi_P(\mathbf{x}) = \phi_p(\mathbf{r})\tau(\sigma) = \phi_{p\tau}$. The theory of second quantization holds unchanged; for example the basic anticommutator now becomes

$$[a_{p\tau}^\dagger, a_{q\upsilon}]_+ = \delta_{p\tau,q\upsilon} = \delta_{pq}\delta_{\tau\upsilon}, \tag{A.58}$$

where, for example, $a_{p\tau}^\dagger$ is the creation operator associated with the spin-orbital $\phi_{p\tau}$.

A.5.2 Operators in the orbital basis

We may classify the quantum-mechanical operators according to how they affect the orbital and spin parts of wave functions: *Spin-free operators*, *spin operators* and *mixed operators*.

One-electron are written in the spin-orbital basis as

$$\hat{f} = \sum_{p\tau} \sum_{q\upsilon} f_{p\tau,q\upsilon} a_{p\tau}^\dagger a_{q\upsilon}.$$

The integrals vanish for opposite spins in the case of spin-free (or spinless) operators:

$$\begin{aligned} f_{p\tau,q\upsilon} &= \int \phi_p^*(\mathbf{r})\tau^*(\sigma) f^c(\mathbf{r}) \phi_q(\mathbf{r})\upsilon(\sigma) d\mathbf{r} d\sigma \\ &= \delta_{\tau\upsilon} \int \phi_p^*(\mathbf{r}) f^c(\mathbf{r}) \phi_q(\mathbf{r}) d\mathbf{r} = f_{pq}\delta_{\tau\upsilon} = \sum_{pq} f_{pq} \hat{E}_{pq}, \end{aligned}$$

[2]Hereafter, generic spin functions τ, υ, μ and ν, which may have a value of either α or β, will be encountered. Note the slight difference in the notation with the course text book [26].

where we have introduced the *singlet excitation operator*

$$\hat{E}_{pq} = a^\dagger_{p\alpha} a_{q\alpha} + a^\dagger_{p\beta} a_{q\beta}. \tag{A.59}$$

The two-electron operators are given by

$$\hat{g} = \frac{1}{2} \sum_{pqrs,\tau\upsilon\mu\nu} g_{p\tau,q\upsilon,r\mu,s\nu} a^\dagger_{p\tau} a^\dagger_{r\mu} a_{s\nu} a_{q\upsilon}.$$

Here, the orthogonality of the spin functions reduce the integrals to

$$g_{p\tau,q\upsilon,r\mu,s\nu} = g_{pqrs} \delta_{\tau\upsilon} \delta_{\mu\nu}, \tag{A.60}$$

where g_{pqrs} are the two-electron integrals in ordinary space, that are always symmetric with respect to the particle-interchange, $g_{pqrs} = g_{rspq}$, and have the Hermitian symmetry $g_{pqrs} = g^*_{qpsr}$ in the case of complex orbitals; and in the case of real orbitals, we have a permutational symmetry

$$g_{pqrs} = g_{qprs} = g_{pqsr} = g_{qpsr}.$$

The second-quantization representation of a spin-free two-electron operator is then

$$\hat{g} = \frac{1}{2} \sum_{pqrs} g_{pqrs} \sum_{\tau\upsilon} a^\dagger_{p\tau} a^\dagger_{r\upsilon} a_{s\upsilon} a_{q\tau} = \frac{1}{2} \sum_{pqrs} g_{pqrs} (\hat{E}_{pq} \hat{E}_{rs} - \delta_{qr} E_{ps}) = \frac{1}{2} \sum_{pqrs} g_{pqrs} \hat{e}_{pqrs}. \tag{A.61}$$

We have introduced the *two-electron singlet excitation operator* in the last equality.

We can now express the spin-free, non-relativistic molecular electronic Hamiltonian in the orbital basis:

$$\hat{H} = \sum_{pq} h_{pq} \hat{E}_{pq} + \frac{1}{2} \sum_{pqrs} g_{pqrs} \hat{e}_{pqrs}. \tag{A.62}$$

The one- and two-electron integrals are the same as in (A.31), except that the integrations are over the spatial coordinates only.

The one-electron second-quantization operators associated to operators that work in spin space only may be written in the general form

$$\begin{aligned} \hat{f} &= \sum_{p\tau q\upsilon} \int \phi^*_p(\mathbf{r}) \tau^*(\sigma) f^c(\sigma) \phi_q(\mathbf{r}) \upsilon(\sigma) d\mathbf{r} d\sigma a^\dagger_{p\tau} a_{q\upsilon} \\ &= \sum_{\tau\upsilon} \int \tau^*(\sigma) f^c(\sigma) \upsilon(\sigma) d\sigma \sum_p a^\dagger_{p\tau} a_{p\upsilon}. \end{aligned} \tag{A.63}$$

Three important examples of pure spin operators are the *raising and lowering operators* $\hat{S}^c_+$ and $\hat{S}^c_-$, and $\hat{S}^c_z$. The effect of these operators on the (one-particle state) spin functions is

$$\begin{aligned} S^c_+ \beta &= \alpha \qquad & \hat{S}^c_+ \alpha &= 0 \\ S^c_- \beta &= 0 \qquad & \hat{S}^c_- \alpha &= \beta \\ S^c_z \beta &= -\frac{1}{2} \beta \qquad & \hat{S}^c_z \alpha &= +\frac{1}{2} \alpha. \end{aligned}$$

From these we arrive at the following expressions for the basic spin operators:

$$\hat{S}_+ = \sum_p a^\dagger_{p\alpha} a_{p\beta} \tag{A.64}$$

$$\hat{S}_- = \sum_p a^\dagger_{p\beta} a_{p\alpha} \tag{A.65}$$

$$\hat{S}_z = \frac{1}{2} \sum_p \left(a^\dagger_{p\alpha} a_{p\alpha} - a^\dagger_{p\beta} a_{p\beta} \right). \tag{A.66}$$

The lowering operator is seen to be the Hermitian adjoint of the raising operator:

$$\hat{S}^\dagger_+ = \sum_p (a^\dagger_{p\alpha} a_{p\beta})^\dagger = \sum_p a^\dagger_{p\beta} a_{p\alpha} = \hat{S}_-.$$

The operators for the x and y components of the spin angular momentum can be written in terms of the raising and lowering operators as

$$\begin{aligned} S^c_x &= \frac{1}{2} \left(S^c_+ + S^c_- \right) \\ S^c_y &= \frac{1}{2i} \left(S^c_+ - S^c_- \right), \end{aligned}$$

from which we obtain the second-quantization counterparts,

$$\hat{S}_x = \frac{1}{2} \sum_p \left(a^\dagger_{p\alpha} a_{p\beta} + a^\dagger_{p\beta} a_{p\alpha} \right) \tag{A.67}$$

$$\hat{S}_y = \frac{1}{2i} \sum_p \left(a^\dagger_{p\alpha} a_{p\beta} - a^\dagger_{p\beta} a_{p\alpha} \right), \tag{A.68}$$

which may be combined with (A.66) to give the operator for the total spin, $\hat{S}^2 = \hat{S}^2_x + \hat{S}^2_y + \hat{S}^2_z$. As it contains products of one-electron operators, it is a two-electron operator and therefore somewhat tedious to manipulate. However, the explicit form is seldom needed, because we are able to employ the standard operator identities:

In contrast to the orbital basis, the spin basis is *complete*, hence the usual first-quantization commutation relations hold also for the second-quantization spin operators. One such example is

$$[\hat{S}_+, \hat{S}_-] = \left[\sum_p a^\dagger_{p\alpha} a_{p\beta}, \sum_q a^\dagger_{q\beta}, a_{q\alpha} \right] = \sum_p \left(a^\dagger_{p\alpha} a_{p\alpha} - a^\dagger_{p\beta} a_{p\beta} \right) = 2\hat{S}_z. \tag{A.69}$$

For example, the fine-structure and hyperfine-structure operators of first quantization affect both the spatial and spin parts of the wave function. An example would be the spin-orbit interaction operator (see Section 7.3.2)

$$V^c_{\mathrm{SO}} = \sum_{i=1}^{N} \xi(r_{iK}) \boldsymbol{\ell}^c_i \cdot \mathbf{S}^c_i.$$

The second-quantization representation is obtained in the usual manner as

$$\begin{aligned}\hat{V}_{\mathrm{SO}} &= \sum_{p\tau q\upsilon}\int \phi_p^*(\mathbf{r})\tau^*(\sigma)V_{\mathrm{SO}}^c(\mathbf{r},\sigma)\phi_q(\mathbf{r})\upsilon(\sigma)d\mathbf{r}d\sigma a_{p\tau}^\dagger a_{q\upsilon} \\ &= \sum_{pq}\left(V_{pq}^x\hat{T}_{pq}^x + V_{pq}^y\hat{T}_{pq}^y + V_{pq}^z\hat{T}_{pq}^z\right), \end{aligned} \tag{A.70}$$

where ($\delta = x, y,$ or z)

$$V_{pq}^\delta = \int \phi_p^*(\mathbf{r})\xi(r)\ell_\delta^c\phi_q(\mathbf{r})d\mathbf{r}$$

and where the Cartesian components of the *triplet excitation operators* are given by

$$\hat{T}_{pq}^x = \frac{1}{2}\left(a_{p\alpha}^\dagger a_{q\beta} + a_{p\beta}^\dagger a_{q\alpha}\right) \tag{A.71}$$

$$\hat{T}_{pq}^y = \frac{1}{2i}\left(a_{p\alpha}^\dagger a_{q\beta} - a_{p\beta}^\dagger a_{q\alpha}\right) \tag{A.72}$$

$$\hat{T}_{pq}^z = \frac{1}{2}\left(a_{p\alpha}^\dagger a_{q\alpha} - a_{p\beta}^\dagger a_{q\beta}\right). \tag{A.73}$$

The second-quantization representation of

- spin-free operators depend on the orbitals but have the same amplitudes (=integrals) for alpha and beta spins
- pure spin operators are independent of the functional form of the orbitals
- mixed operators depend on both the spin of the electron and the functional form of the orbitals.

A.5.3 Spin properties of determinants

Slater determinants are in general not eigenfunctions of the non-relativistic Hamiltonian (A.62), but are instead non-degenerate eigenfunctions of the spin-orbital occupation-number operators:

$$\hat{N}_{p\sigma}\left|\mathbf{k}\right\rangle = k_{p\sigma}\left|\mathbf{k}\right\rangle. \tag{A.74}$$

We also note that the spin-orbital ON operators commute with the spin-projection operator, i.e. $[\hat{S}_z, \hat{N}_{p\sigma}] = 0$, because the ON operators commute among themselves, and $\hat{S}_z$ is a linear combination of spin-orbital ON operators. Added by the observation that there is no degeneracies in (A.74), the Slater determinants are eigenfunctions of the *projected* spin:

$$\hat{S}_z\left|\mathbf{k}\right\rangle = M\left|\mathbf{k}\right\rangle. \tag{A.75}$$

By contrast, the Slater determinants are not eigenfunctions of the *total* spin. However, it is possible to determine spin eigenfunctions as simple linear combinations of determinants.

A hint for the procedure is given by an observation that both the total and projected-spin operators commute with the *sum* of the ON operators for alpha and beta spins:

$$\begin{aligned}\left[\hat{S}_z, \hat{N}_{p\sigma} + \hat{N}_{p\beta}\right] &= 0 \\ \left[\hat{S}^2, \hat{N}_{p\sigma} + \hat{N}_{p\beta}\right] &= 0,\end{aligned}$$

because $\hat{N}_{p\sigma} + \hat{N}_{p\beta}$ are singlet operators. Such spin-adapted functions are known as *configuration state functions*.

Appendix B

Performance of the electronic-structure models

Having now considered the most important approximations to the molecular electronic wave function we will now address their performance in terms of a few numerical examples [26]. It should be remembered that none of these models (besides FCI, which is inapplicable for most cases) is an all-around-good one: good performance in some problem and/or in some system does not guarantee good performance in another situation.

B.1 Total electronic energies

For the total molecular energy, i.e., E in the molecular Schrödinger equation, there is no direct experimental counterpart. We examine it in order to establish a feeling on the severity of the approximations involved in the calculation. We should recall that there were a third class of approximations in addition to the truncation of one- and N-electron spaces: approximations in the molecular Hamiltonian $\hat{H}$. To investigate the validity of the use of the non-relativistic Hamiltonian, we include the leading-order one-electron relativistic corrections that include the spin-orbit interaction (SO) (7.32), mass-velocity (MV) , and the Darwin (Dar) corrections, see Table 7.3.2. The leading-order two-electron contributions, such as the two-electron Darwin contribution and the spin-spin contact interaction, are smaller by at least one order of magnitude. The MV and Dar corrections are always of opposite sign. The calculation is carried out using the CCSDT model for the water molecule in the cc-pCVXZ bases at a CCSD(T)/cc-pCVQZ geometry and presented in Table B.1.

Some observations:

- It is remarkable how a tiny, less than one per cent fraction of the total energy, plays such an important role in the determination of molecular properties.
- The leading-order relativistic correction, -52.18 mE_h, is larger than the triples contribution already in water, and gets far more pronounced in systems with heavier

elements present!

- (T) is a very good approximation to full triples.

	Total energy [E_h]		Energy corrections [mE_h]					
	CCSDT	HF	HF→SD	SD→(T)	(T)→T	SO	MV	Dar
DZ	-76.24121	-76.02680	-211.21	-3.04	-0.16			
TZ	-76.33228	-76.05716	-267.40	-7.65	-0.08			
QZ	-76.35981	-76.06482	-285.98	-8.99	-0.01	0.00	-255.87	203.69
5Z	-76.36899	-76.06708	-292.44	-9.52	0.04			

Table B.1: Breakdown of the total electronic energy of water molecule.

B.2 Molecular equilibrium geometries

One of the most common applications of molecular electronic-structure calculations is the determination of the molecular equilibrium structures. Good geometries are also of fundamental importance in study of molecular properties.

We consider the mean errors and standard deviations of calculated bond distances and bond angles as compared to experimental results using a hierarchy of N-electron models and a hierarchy of Gaussian basis sets. The error is given by $\Delta = P_i^{\text{calc}} - P_i^{\text{exp}}$, and the mean error and standard deviation by

$$\bar{\Delta} = \frac{1}{n}\sum_{i=1}^{n}\Delta_i \tag{B.1}$$

$$\Delta_{\text{std}} = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(\Delta_i - \bar{\Delta})^2}. \tag{B.2}$$

They can be conveniently represented graphically in terms of the normal distribution

$$\rho(P) = N_c \exp\left[-\frac{1}{2}\left(\frac{P-\bar{\Delta}}{\Delta_{\text{std}}}\right)^2\right]. \tag{B.3}$$

The calculations were carried out for sets of small molecules containing main-group elements. 29 bond distances and 10 bond angles were calculated and presented in Figures B.1 and B.2, respectively. Figure B.3 illustrate the convergence of the hierarchy of correlation models.

Some observations:

- The Hartree–Fock model is suitable for only preliminary calculations.

- The CCSD(T) model is capable of providing structures – both bond distances and angles – of high quality.
- The MP2 model is less accurate but more generally applicable as it is considerably less expensive. Higher-order MPPT is significantly less accurate but hideously expensive, i.e., useless.
- The performance of the CCSD model is disappointing. It however performs more robust than MP2 in some selected cases with complicated electronic structure.
- The CISD model is also rather useless, showing no improvement when the basis set is increased.
- The basis-set requirements are different for different models. Whereas there is no much use to use QZ-level basis sets with the Hartree–Fock model (as the results are not improved), the correlated models require at least a TZ-level basis set, but preferably the cc-pVQZ basis.

The results suggest the following recipe for the determination of molecular structures: obtain an initial structure with HF using a DZ-level basis and improve it by using MP2 and a TZ basis. If ever possible, calculate the final geometry in the cc-pVQZ basis using the CCSD(T) model.

B.3 Molecular dipole moments

The comparison between the experimental and calculated molecular dipole moments is difficult, as the experiments are measuring the dipole moment in the vibrational ground state μ_0, whereas the calculations are carried out for the equilibrium dipole moment μ_e, and thus we would have to carry out a vibrational averaging in order to speak of the same quantity. However, there are a few experimental values for μ_e, and we shall compare the performance of our standard models with those, reported in Table B.3. Note, that due to the outer-valence origin of this property, we have to augment our basis sets with extra diffuse primitive Gaussians; hence we are using the aug-cc-pVXZ basis sets. The geometries are optimized using the same wave function as for the calculation of the dipole moment.

The quality of the calculation is more dependent on the correlation treatment than the cardinal number of the basis set; yet it is necessary to augment the basis set. The further augmentation (d-aug-cc-pVXZ basis sets) of the basis set does not affect the calculated dipole moments significantly.

B.4 Reaction enthalpies

Last, we study the reaction enthalpies of 13 chemical reactions among closed-shell molecules. The calculations are carried out in the HF–MP2–CCSD–CCSD(T) hierarchy, using the

	Exp.	HF	MP2	CCSD	CCSD(T)		
		QZ	QZ	QZ	DZ	TZ	QZ
NH_3	1.561(5)	1.544	1.517	1.530	1.541	1.513	1.521
HF	1.803(2)	1.884	1.811	1.813	1.799	1.797	1.800
H_2O	1.8473(10)	1.936	1.864	1.870	1.859	1.845	1.853

Table B.2: Molecular dipole moments by experiment and theory.

correlation-consistent basis set hierarchy supplemented with steep functions to provide core-polarization, which – somewhat surprisingly – must be included in the high-precision calculation of reaction enthalpies.

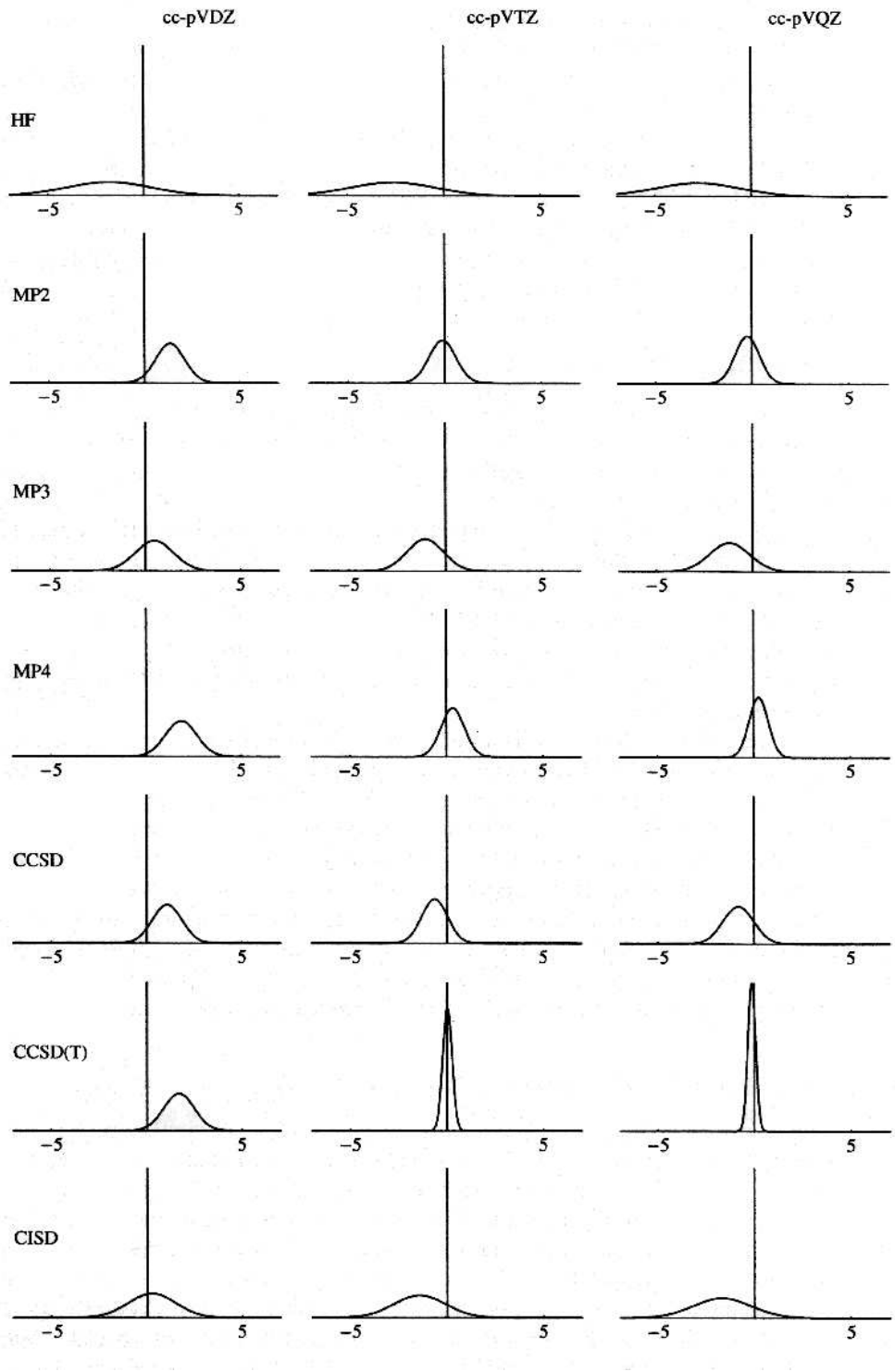


Figure B.1: Errors in the calculated bond lengths of 29 molecules as a function of the level of theory.

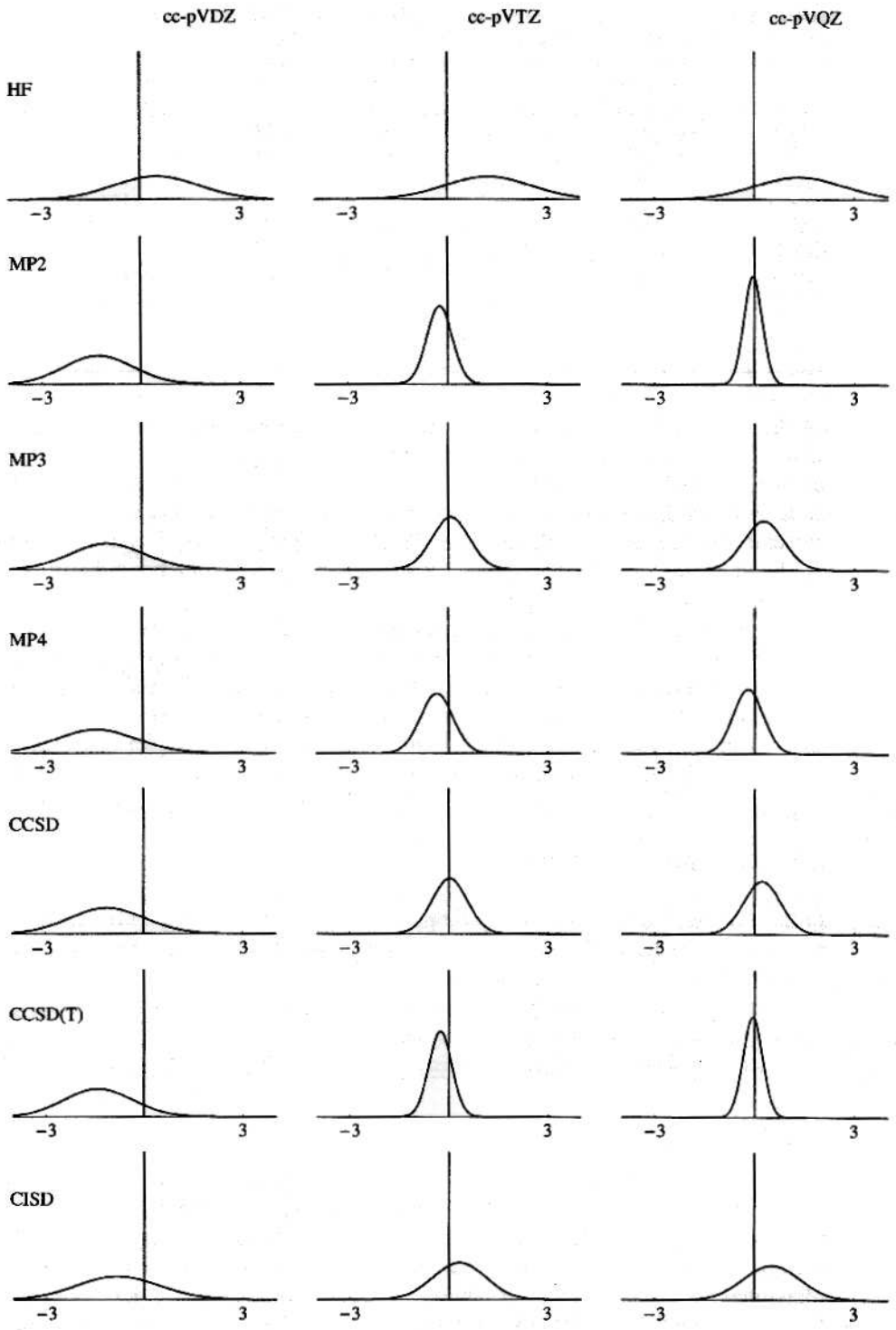


Figure B.2: Errors in the calculated bond angles of 13 molecules as a function of the level of theory.

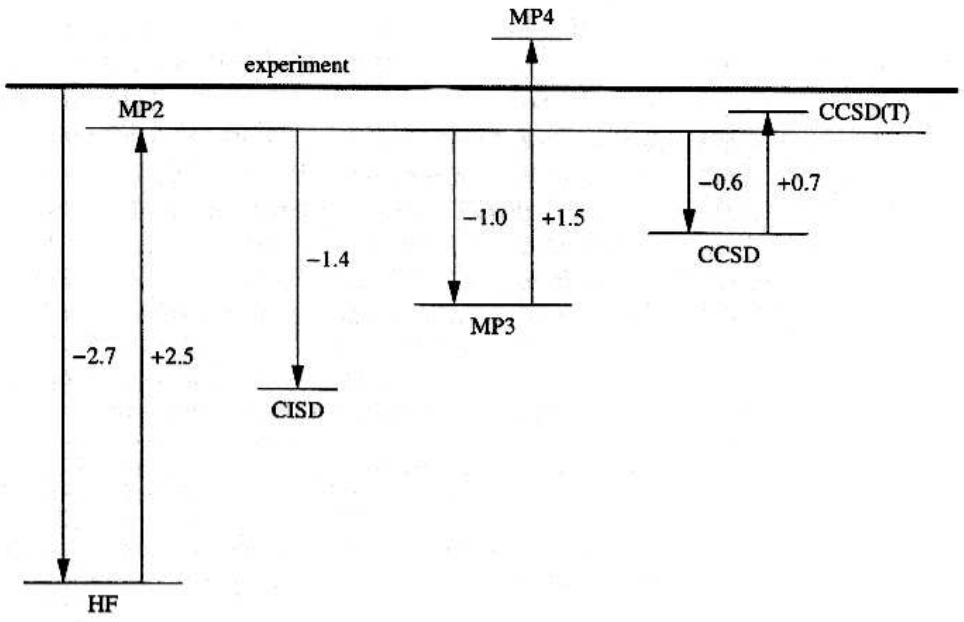


Figure B.3: Changes in bond lengths calculated from $\bar{\Delta}$ of the cc-pVQZ basis.

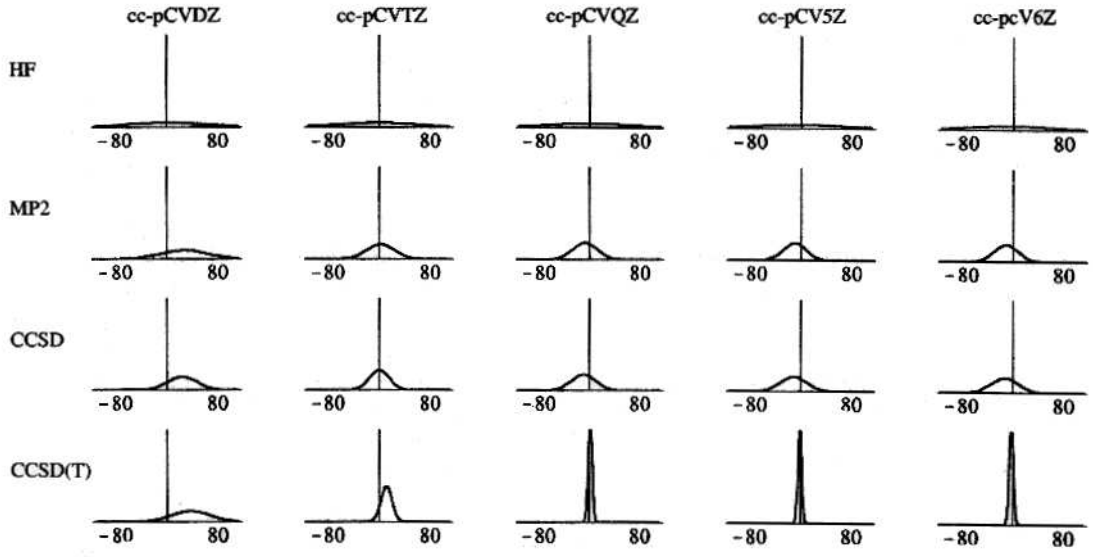


Figure B.4: Performance of different models in computation of reaction enthalpies.

References

[1] R. McWeeny, *Methods of Molecular Quantum Mechanics, 2nd edition.* Academic Press, London, 1992.

[2] P. W. Atkins and R. S. Friedman, *Molecular Quantum Mechanics, 3rd edition.* Oxford University Press, Oxford, 1997.

[3] R. E. Moss, *Advanced Molecular Quantum Mechanics.* Chapman & Hall, 1973.

[4] J. Olsen and P. Jørgensen in *Modern Electronic Structure Theory, Part II* (D. R. Yarkony, ed.), World Scientific, Singapore, 1995.

[5] T. L. Beck *Rev. Mod. Phys.*, vol. 72, p. 1041, 2000.

[6] R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules.* Oxford University Press, Oxford, 1989.

[7] P.-O. Löwdin *Rev. Mod. Phys.*, vol. 34, p. 80, 1962.

[8] C. C. J. Roothaan *Rev. Mod. Phys.*, vol. 23, p. 69, 1951.

[9] G. G. Hall *Proc. Roy. Soc. A*, vol. 208, p. 328, 1951.

[10] P. Pulay *J. Chem. Phys.*, vol. 73, p. 393, 1980.

[11] P. Pulay *J. Comp. Chem.*, vol. 4, p. 556, 1982.

[12] H. Sellers *Int. J. Quantum Chem.*, vol. 45, p. 31, 1993.

[13] K. N. Kudin, G. E. Scuseria, and E. Cancés *J. Chem. Phys.*, vol. 116, p. 8255, 2002.

[14] P. Salek, S. Reine, F. Pawlowski, T. Helgaker, S. Høst, L. Thøgersen, P. M. P. Jørgensen, J. Olsen, B. Jansík, and S. Coriani *J. Chem. Phys.*, vol. 126, p. 114110, 2007.

[15] J. Almlöf, K. Fægri, and K. Korsell *J. Comp. Chem.*, vol. 3, p. 385, 1982.

[16] M. C. Strain, G. E. Scuseria, and M. J. Frisch *Science*, vol. 271, p. 51, 1996.

[17] C. Møller and M. S. Plesset *Phys. Rev.*, vol. 46, p. 618, 1934.

[18] J. A. Pople, J. S. Binkley, and R. Seeger *Int. J. Quantum Chem. Symp.*, vol. 10, p. 1, 1976.

[19] I. Shavitt in *Methods of Electronic Structure Theory* (H. F. S. III, ed.), Plenum Press, New York, 1977.

[20] B. O. Roos, P. R. Taylor, and P. E. M. Siegbahn *Chem. Phys.*, vol. 48, p. 157, 1980.

[21] J. Olsen, B. O. Roos, P. Jørgensen, and H. J. A. Jensen *J. Chem. Phys.*, vol. 89, p. 2185, 1988.

[22] P.-Å. Malmqvist, A. Rendell, and B. O. Roos *J. Chem. Phys.*, vol. 94, p. 5477, 1990.

[23] A. C. Hurley, *Electron correlation in small molecules.* Academic Press, London, 1976.

[24] C. D. Purvis and R. J. Bartlett *J. Chem. Phys.*, vol. 76, p. 1910, 1982.

[25] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon *Chem. Phys. Lett.*, vol. 157, p. 479, 1989.

[26] T. Helgaker, P. Jørgensen, and J. Olsen, *Molecular Electronic-Structure Theory.* John Wiley & Sons, Chichester, 2000.

[27] J. Noga and R. J. Bartlett *J. Chem. Phys.*, vol. 86, p. 7041, 1987.

[28] K. Andersson, P.-Å. Malmqvist, B. O. Roos, A. J. Sadlej, and K. Wolinski *J. Phys. Chem.*, vol. 94, p. 5483, 1990.

[29] P. Pulay *Chem. Phys. Lett.*, vol. 100, p. 151, 1983.

[30] S. Sæbø and P. Pulay *Annu. Rev. Phys. Chem.*, vol. 44, p. 213, 1993.

[31] P. E. Maslen, C. Ochsenfeld, C. A. White, M. S. Lee, and M. Head-Gordon *J. Phys. Chem. A*, vol. 102, p. 2215, 1998.

[32] G. E. Scuseria and P. Y. Ayala *J. Chem. Phys.*, vol. 111, p. 8330, 1999.

[33] P. Y. Ayala and G. E. Scuseria *J. Chem. Phys.*, vol. 110, p. 3660, 1999.

[34] C. Hampel and H. J. Werner *J. Chem. Phys.*, vol. 104, p. 6286, 1996.

[35] M. Schütz, G. Hetzer, and H.-J. Werner *J. Chem. Phys.*, vol. 111, p. 5691, 1999.

[36] M. Schütz and H.-J. Werner *J. Chem. Phys.*, vol. 114, p. 661, 2001.

[37] M. Schutz *Chem. Phys. Phys. Chem.*, vol. 4, p. 3941, 2002.

[38] H. J. Werner, F. R. Manby, and P. J. Knowles *J. Chem. Phys.*, vol. 118, p. 8149, 2003.

[39] J. E. Subotnik and M. Head-Gordon *J. Chem. Phys.*, vol. 122, p. 034109, 2005.

[40] P. E. Maslen, A. D. Dutoi, M. S. Lee, Y. H. Shao, and M. Head-Gordon *Mol. Phys.*, vol. 103, p. 425, 2005.

[41] O. Christiansen, P. Manninen, P. Jørgensen, and J. Olsen *J. Chem. Phys.*, vol. 124, p. 084103, 2006.

[42] V. Weijo, P. Manninen, P. Jørgensen, O. Christiansen, and J. Olsen *J. Chem. Phys.*

[43] R. Ditchfield, W. J. Hehre, and J. A. Pople *J. Chem. Phys.*, vol. 54, p. 724, 1971.

[44] R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople *J. Chem. Phys.*, vol. 72, p. 650, 1980.

[45] A. Schäfer, H. Horn, and R. Ahlrichs *J Chem Phys*, vol. 97, p. 2571, (1992).

[46] A. Schäfer, C. Huber, and R. Ahlrichs *J. Chem. Phys.*, vol. 100, p. 5829, 1994.

[47] F. Weigend, F. Furche, and R. Ahlrichs *J. Chem. Phys.*, vol. 119, p. 12753, 2003.

[48] T. H. Dunning *J. Chem. Phys.*, vol. 90, p. 1007, 1989.

[49] R. A. Kendall, T. H. Dunning, and R. J. Harrison *J. Chem. Phys.*, vol. 96, p. 6796, 1992.

[50] D. E. Woon and T. H. Dunning *J. Chem. Phys.*, vol. 98, p. 1358, 1993.

[51] K. A. Peterson, R. A. Kendall, and T. H. Dunning *J. Chem. Phys.*, vol. 99, p. 9790, 1993.

[52] K. A. Peterson, D. E. Woon, and T. H. Dunning *J. Chem. Phys.*, vol. 100, p. 7410, 1994.

[53] A. Wilson, T. van Mourik, and T. H. Dunning *J. Mol. Struct. (THEOCHEM)*, vol. 388, p. 339, 1997.

[54] P.-O. Widmark, P.-Å. Malmqvist, and B. O. Roos *Theor. Chim. Acta*, vol. 77, p. 291, 1990.

[55] P.-O. Widmark, B. J. Persson, and B. O. Roos *Theor. Chim. Acta*, vol. 79, p. 419, 1990.

[56] D. P. Chong *Can. J. Chem.*, vol. 73, p. 79, 1995.

[57] P. Manninen and J. Vaara *J. Comp. Chem.*, vol. 27, p. 434, 2006.

[58] S. Obara and M. Saika *J. Chem. Phys.*, vol. 84, p. 3963, 1986.

[59] S. Obara and M. Saika *J. Chem. Phys.*, vol. 89, p. 1540, 1988.

[60] P. A. M. Dirac *Proc. Roy. Soc. A*, vol. 117, p. 610, 1928.

[61] P. A. M. Dirac *Proc. Roy. Soc. A*, vol. 118, p. 351, 1928.

[62] C. D. Anderson *Phys. Rev.*, vol. 43, p. 491, 1933.

[63] J. M. Lévy-Leblond *Commun. Math. Phys.*, vol. 6, p. 216, 1967.

[64] E. E. Salpeter and H. A. Bethe *Phys. Rev.*, vol. 84, p. 1232, 1951.

[65] E. E. Salpeter *Phys. Rev.*, vol. 87, p. 328, 1952.

[66] J. E. Harriman, *Theoretical Foundations of Electron Spin Resonance*. Academic Press, New York, 1978.

[67] G. Breit *Phys. Rev.*, vol. 34, p. 553, 1929.

[68] J. A. Gaunt *Proc. Roy. Soc. (London) A*, vol. 122, p. 513, 1929.

[69] G. E. Brown and D. G. Ravenhall *Proc. Roy. Soc. (London) A*, vol. 208, p. 55, 1951.

[70] K. G. Dyall and K. Fægri *Chem. Phys. Lett.*, vol. 174, p. 25, 1990.

[71] R. E. Stanton and S. Havriliak *J. Chem. Phys.*, vol. 81, p. 1910, 1984.

[72] L. L. Foldy and S. A. Wouthuysen *Phys. Rev.*, vol. 78, p. 29, 1950.

[73] K. G. Dyall *J. Chem. Phys.*, vol. 106, p. 9618, 1997.

[74] J. Autschbach and W. H. E. Schwarz *Theor. Chem. Acc.*, vol. 104, p. 82, 2000.

[75] W. Pauli in *Handbuch der Physik*, vol. 5, Springer, Berlin, 1958.

[76] D. W. Davies, *The Theory of the Electronic and Magnetic Properties of Molecules*. Wiley, London, 1969.

[77] W. Kutzelnigg *Theor. Chim. Acta*, vol. 73, p. 173, 1988.

[78] J. D. Morrison and R. E. Moss *Mol. Phys.*, vol. 41, p. 491, 1980.

[79] I. J. Ketley and R. E. Moss *Mol. Phys.*, vol. 48, p. 1131, 1983.

[80] I. J. Ketley and R. E. Moss *Mol. Phys.*, vol. 49, p. 1289, 1983.

[81] R. E. Moss *Mol. Phys.*, vol. 53, p. 269, 1984.

[82] A. Farazdel and V. H. Smith *Int. J. Quantum Chem.*, vol. 29, p. 311, 1986.

[83] T. Ziegler, V. Tschinke, E. J. Baerends, J. G. Snijders, and W. Ravenek *J. Phys. Chem.*, vol. 93, p. 3050, 1989.

[84] E. van Lenthe, E. J. Baerends, and J. G. Snijders *J. Chem. Phys.*, vol. 99, p. 4597, 1993.

[85] C. Chang, M. Pelissier, and P. Durand *Phys. Scr.*, vol. 34, p. 394, 1986.

[86] R. van Leeuwen, E. van Lenthe, A. Ehlers, E. J. Baerends, and J. G. Snijders *J. Chem. Phys.*, vol. 101, p. 1272, 1994.

[87] M. Barysz and A. J. Sadlej *Theor. Chim. Acta*, vol. 97, p. 260, 1997.

[88] D. Sundholm *Theor. Chem. Acc.*, vol. 110, p. 144, 2002.

[89] A. J. Sadlej and J. G. Snijders *Chem. Phys. Lett.*, vol. 229, p. 435, 1994.

[90] K. G. Dyall and E. van Lenthe *J. Chem. Phys.*, vol. 111, p. 1366, 1999.

[91] M. Filatov and D. Cremer *J. Chem. Phys.*, vol. 119, p. 11526, 2003.

[92] B. A. Hess *Phys. Rev. A*, vol. 32, p. 756, 1985.

[93] B. A. Hess *Phys. Rev. A*, vol. 33, p. 3742, 1986.

[94] J. Sucher *Phys. Rev. A*, vol. 22, p. 348, 1980.

[95] M. Douglas and N. M. Kroll *Ann. Phys. (N.Y.)*, vol. 82, p. 89, 1974.

[96] J. G. Snijders and A. J. Sadlej *Chem. Phys. Lett.*, vol. 252, p. 51, 1996.

[97] M. Baryz, A. J. Sadlej, and J. G. Snijders *Int. J. Quantum Chem.*, vol. 65, p. 225, 1997.

[98] T. Nakajima and K. Hirao *Chem. Phys. Lett.*, vol. 302, p. 383, 1999.

[99] L. Visscher and T. Saue *J. Chem. Phys.*, vol. 113, p. 3996, 2000.

[100] F. Wang, G. Hong, and L. Li *Chem. Phys. Lett.*, vol. 316, p. 318, 2000.

[101] D. G. Fedorov, T. Nakajima, and K. Hirao *Chem. Phys. Lett.*, vol. 335, p. 183, 2001.

[102] M. Filatov and D. Cremer *Chem. Phys. Lett.*, vol. 351, p. 259, 2002.

[103] G. L. Sewell *Proc. Cambridge Phil. Soc.*, vol. 45, p. 631, 1949.

[104] A. Rutkowski *J. Phys. B*, vol. 19, pp. 149, *Ibid.* 3431, *Ibid.* 3443, 1986.

[105] W. Kutzelnigg *Z. Phys. D*, vol. 11, p. 15, 1989.

[106] M. Dolg in *Modern Methods and Algorithms of Quantum Chemistry* (J. Grotendorst, ed.), vol. 1, John von Neumann Institute for Computing, Jülich, 2002.

[107] P. Pyykkö and H. Stoll in *Chemical Modelling: Applications and Theory* (A. Hinchliffe, ed.), vol. 1, R. S. C., Cambridge, 2000.

[108] P. Jørgensen and J. Simons, *Second Quantization Based Methods in Quantum Chemistry.* Academic Press, New York, 1981.