Chapter 1
Basic Concepts

Abstract In this chapter we examine some basic concepts of quantum chemistry to give a solid foundation for the other chapters. We do not pretend to review all the basics of quantum mechanics but rather focus on some specific topics that are central in the theoretical description of magnetic phenomena in molecules and extended systems. First, we will shortly review the Slater–Condon rules for the matrix elements between Slater determinants, then we will extensively discuss the generation of spin functions. Perturbation theory and effective Hamiltonians are fundamental tools for understanding and to capture the complex physics of open shell systems in simpler concepts. Therefore, the last three sections of this introductory chapter are dedicated to standard Rayleigh–Schrödinger perturbation theory, quasi-degenerate perturbation theory and the construction of effective Hamiltonians.

1.1 Slater Determinants and Slater–Condon Rules

The Slater determinant is the central entity in molecular orbital theory. The exact N-electron wave function of a stationary molecule in the Born-Oppenheimer approximation is a $4N$-dimensional object that depends on the three spatial coordinates and a spin coordinate of the N electrons in the system. This object is of course too complicated for any practical application and is, in first approximation, replaced by a product of N orthonormal 4-dimensional functions that each depend on the coordinates of only one of the electrons in the system.

$$\begin{aligned} &\Psi(x_1, y_1, z_1, \sigma_1, x_2, y_2, z_2, \sigma_2, \ldots, x_N, y_N, z_N, \sigma_N) \\ &\quad = \phi_a(x_1, y_1, z_1, \sigma_1)\phi_b(x_2, y_2, z_2, \sigma_2)\ldots\phi_\omega(x_N, y_N, z_N, \sigma_N) \end{aligned} \tag{1.1}$$

These one-electron functions are commonly referred to as spin orbitals and the product is known as the Hartree product Π. Obviously, the product suffers from important deficiencies with respect to the foundations of Quantum Mechanics. The wave function is not antisymmetric with respect to the permutation of any two electrons, and

C. Graaf and R. Broer, *Magnetic Interactions in Molecules and Solids*,
Theoretical Chemistry and Computational Modelling,
DOI 10.1007/978-3-319-22951-5_1

hence, does not fulfill the Pauli principle. However, by replacing the product by a determinant

$$\Psi(1,2,\dots N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_a(1) & \phi_b(1) & \cdots & \phi_\omega(1) \\ \phi_a(2) & \phi_b(2) & \cdots & \phi_\omega(2) \\ \vdots & & & \vdots \\ \phi_a(N) & \phi_b(N) & \cdots & \phi_\omega(N) \end{vmatrix} \tag{1.2}$$

this requirement is automatically fulfilled. Shorthand notations for this Slater determinant are

$$\Psi(1,2,\dots N) = |\phi_a(1)\phi_b(2)\dots\phi_\omega(N)| = |\phi_a\phi_b\dots\phi_\omega| \tag{1.3}$$

where only the diagonal elements of the determinant are shown, the four coordinates are compacted in one index, and the normalization factor is implicit. The one-electron functions are ordered by columns *(from left to right)* and the electrons by rows *(from top to bottom)*. An alternative, more explicit way of writing the wave function is obtained by defining an operator that antisymmetrizes the Hartree product Π

$$\Psi = \hat{A}\Pi = \hat{A}[\phi_a(1)\phi_b(2)\dots\phi_\omega(N)] \tag{1.4}$$

with

$$\hat{A} = \frac{1}{\sqrt{N!}} \sum_{\gamma=0}^{N-1} (-1)^\gamma \hat{P}_\gamma = \frac{1}{\sqrt{N!}} \left(1 - \sum_{i<j} \hat{P}_{ij} + \sum_{i<j<k} \hat{P}_{ijk} - \dots\right) \tag{1.5}$$

where $\hat{P}_{ij}$ permutes the electron labels i and j in the Hartree product, $\hat{P}_{ijk}$ replaces the electron labels ijk by jki and kij.

1.1 Write out explicitly the wave function $\Psi(1,2,3) = |\phi_a(1)\phi_b(2)\phi_c(3)|$ and show that $\Psi(2,1,3) = -\Psi(1,2,3)$. What happens to the wave function when two electrons are described by the same one-electron function?

A serious deficiency is that neither a Hartree product nor a Slater determinant can be an eigenfunction of the N-electron Hamilton operator. Therefore Ψ cannot be a solution of the time-independent electronic Schrödinger equation. The reason is that the N-electron Hamiltonian cannot be written as a sum of N one-electron Hamiltonians, due to the repulsive Coulomb interactions between the electrons. Nevertheless, in practice it turns out that we can work rather well with an approximate wave function consisting of only one Slater determinant if we choose that particular Slater determinant Ψ that yields the lowest energy expectation value $\langle\Psi|\hat{H}|\Psi\rangle$. In other words, we must vary the spin orbitals in Ψ until we have reached the lowest value of $\langle\Psi|\hat{H}|\Psi\rangle$. The variation theorem tells us that this lowest value is still above the exact ground state energy E.

This variational procedure leads to a set of equations

$$\hat{f}\phi_i = \varepsilon_i\phi_i \tag{1.6}$$

called the Hartree–Fock equations, which determine the spin orbitals in Ψ. The set of equations (1.6) can be seen as effective one-electron Schrödinger equations, whose eigenvalues ε are called one-electron energies or orbital energies. There is an operator $\hat{f}$, called Fock operator, for each electron in the molecule, and they are all identical. Much can be said about the Hartree–Fock equations, their eigenvalues ε and their eigenfunctions, the spin orbitals ϕ but here we restrict ourselves to a few aspects that are relevant later in this chapter. Firstly, $\hat{f}$ depends on the spin orbitals to be found, which has the consequence that the equations have to be solved iteratively and secondly, the energy expectation value E is not equal to the sum of the one electron energies. Summing the N individual Fock operators for the electrons of the molecule gives an N-electron Hamiltonian, $\hat{H}^{(0)}$, that is not equal to the true N-electron Hamiltonian, but that we will use later as zeroth order Hamiltonian in a perturbation expansion. All Slater determinants Φ_k, $k = 1, 2, \ldots$ that can be built from the spin orbitals of Eq. 1.6 are eigenfunctions of $\hat{H}^{(0)}$, with eigenvalues $E_k^{(0)}$ equal to the sum of the orbital energies of the spin orbitals used in Ψ_k.

The calculation of the energy of a Slater determinant and the interaction between two different Slater determinants may seem a rather complicated task given the large number of terms ($N!$) when the determinant is written in its explicit form. However, the Slater–Condon rules given in Table 1.1 establish a few simple relations to calculate matrix elements between two Slater determinants.

Table 1.1 Slater–Condon rules for the matrix elements between two Slater determinants

Matrix element	Differences	One-electron term	Two-electron term
$\langle\Phi_K\vert\hat{H}\vert\Phi_K\rangle$	0	$\sum_{m}^{N}\langle\phi_m\vert\hat{h}\vert\phi_m\rangle$	$\sum_{m<n}^{N}\langle\phi_m\phi_n\vert\frac{1-\hat{P}_{12}}{r_{12}}\vert\phi_m\phi_n\rangle$
$\langle\Phi_K\vert\hat{H}\vert\Phi_L\rangle$	1	$\langle\phi_m\vert\hat{h}\vert\phi_p\rangle$	$\sum_{n}^{N}\langle\phi_m\phi_n\vert\frac{1-\hat{P}_{12}}{r_{12}}\vert\phi_p\phi_n\rangle$
$\langle\Phi_K\vert\hat{H}\vert\Phi_M\rangle$	2	0	$\langle\phi_m\phi_n\vert\frac{1-\hat{P}_{12}}{r_{12}}\vert\phi_p\phi_q\rangle$
$\langle\Phi_K\vert\hat{H}\vert\Phi_N\rangle$	3 or more	0	0

The entry ‘differences’ indicates the number of different spin orbitals in the determinants of the *bra* and *ket*

$\Phi_K = |\phi_a\phi_b\ldots\phi_m\phi_n\phi_o\ldots\phi_\omega|$
$\Phi_L = |\phi_a\phi_b\ldots\phi_p\phi_n\phi_o\ldots\phi_\omega|$
$\Phi_M = |\phi_a\phi_b\ldots\phi_p\phi_q\phi_o\ldots\phi_\omega|$
$\Phi_N = |\phi_a\phi_b\ldots\phi_p\phi_q\phi_r\ldots\phi_\omega|$

$\hat{P}_{12}$ is the permutation operator that interchanges the coordinates of electron 1 and 2

To derive these rules it is convenient to introduce two formal properties of the antisymmetrizer $\hat{A}$

$$\hat{A}\hat{A} = \sqrt{N!}\hat{A} \qquad \hat{A}\hat{H} = \hat{H}\hat{A} \tag{1.7}$$

where $\hat{H}$ is the many-electron Hamiltonian.

1.2 Write down the anti-symmetrization operator $\hat{A}$ for a two-particle wave function. Show that $\hat{A}\hat{A}$ applied on the Hartree product $\varphi_1\varphi_2$ gives the same result as applying $\sqrt{N!}\hat{A}$.

Then the energy of the determinant Φ_K can be written as

$$E = \langle \Phi_K|\hat{H}|\Phi_K\rangle = \langle \hat{A}\Pi|\hat{H}|\hat{A}\Pi\rangle = \sqrt{N!}\langle \Pi|\hat{H}|\hat{A}\Pi\rangle = \sum_{\gamma=0}^{N-1}(-1)^{\gamma}\langle \Pi|\hat{H}|\hat{P}_{\gamma}\Pi\rangle \tag{1.8}$$

and instead of working with determinants, the energy can be calculated from the Hartree products. In the first place, we take a closer look on the one-electron part of the Hamiltonian. For $\gamma = 0$ and $\hat{h}(1)$ we obtain

$$\begin{aligned}&\langle \phi_a(1)\phi_b(2)\dots\phi_\omega(N)|\hat{h}(1)|\phi_a(1)\phi_b(2)\dots\phi_\omega(N)\rangle \\ &= \langle \phi_a(1)|\hat{h}(1)|\phi_a(1)\rangle\langle \phi_b(2)\dots\phi_\omega(N)|\phi_b(2)\dots\phi_\omega(N)\rangle = \langle \phi_a|\hat{h}|\phi_a\rangle = h_a\end{aligned} \tag{1.9}$$

Using $\hat{h}(2)$ leads to h_b and all other electron coordinates give similar results. On the contrary, the evaluation of the matrix elements with $\gamma = 1$, that is one permutation in Π, leads to zero due to the orthogonality of the orbitals. For example, the action of $\hat{P}_{12}$ gives

$$\begin{aligned}&-\langle \phi_a(1)\phi_b(2)\dots\phi_\omega(N)|\hat{h}(1)|\phi_b(1)\phi_a(2)\dots\phi_\omega(N)\rangle \\ &= -\langle \phi_a(1)|\hat{h}(1)|\phi_b(1)\rangle\langle \phi_b(2)\dots\phi_\omega(N)|\phi_a(2)\dots\phi_\omega(N)\rangle = 0\end{aligned} \tag{1.10}$$

where the minus sign arises from the $(-1)^{\gamma}$ factor in the energy expression. The two-electron part can be determined with a similar reasoning. First we focus on the $\gamma = 0$ case with the coordinates of electron 1 and 2.

$$\begin{aligned}&\langle \phi_a(1)\phi_b(2)\phi_c(3)\dots\phi_\omega(N)|\frac{1}{r_{12}}|\phi_a(1)\phi_b(2)\phi_c(3)\dots\phi_\omega(N)\rangle \\ &= \langle \phi_a(1)\phi_b(2)|\frac{1}{r_{12}}|\phi_a(1)\phi_b(2)\rangle\langle \phi_c(3)\dots\phi_\omega(N)|\phi_c(3)\dots\phi_\omega(N)\rangle \\ &= \langle \phi_a\phi_b|\frac{1}{r_{12}}|\phi_a\phi_b\rangle = J_{ab}\end{aligned} \tag{1.11}$$

Similar Coulomb integrals J are obtained for other combinations of electron coordinates. The next step is to see what integrals are obtained for $\gamma = 1$ interchanging electrons 1 and 2:

$$\begin{aligned}
&-\langle\phi_a(1)\phi_b(2)\phi_c(3)\ldots\phi_\omega(N)|\frac{1}{r_{12}}|\phi_b(1)\phi_a(2)\phi_c(3)\ldots\phi_\omega(N)\rangle \\
&= -\langle\phi_a(1)\phi_b(2)|\frac{1}{r_{12}}|\phi_b(1)\phi_a(2)\rangle\langle\phi_c(3)\ldots\phi_\omega(N)|\phi_c(3)\ldots\phi_\omega(N)\rangle \\
&= -\langle\phi_a\phi_b|\frac{1}{r_{12}}|\phi_b\phi_a\rangle = -K_{ab} \qquad (1.12)
\end{aligned}$$

This integral is known as the exchange integral and usually written as K_{ab}. Other combinations of permutations and electron coordinates lead to similar $K's$ but higher-order permutations will always result in zero contributions due to the orthogonality. Hence, the terms can be collected and the expression given in the top row of Table 1.1 emerges.

The evaluation of the interaction matrix elements between Slater determinants with different occupations follows the same mechanics and can be derived as a useful exercise by the reader.

1.2 Generation of Many Electron Spin Functions

In a non-relativistic setting the N-electron wave function Ψ can be chosen to be also an eigenfunction of $\hat{S}^2$ and one of its components, we denote this component $\hat{S}_z$.

$$\hat{S}^2\Psi_{S,M_S} = S(S+1)\Psi_{S,M_S} \qquad (1.13a)$$

$$\hat{S}_z\Psi_{S,M_S} = M_S\Psi_{S,M_S} \qquad (1.13b)$$

with S the total spin quantum number and the magnetic spin quantum number M_S running from $-S$ to S in steps of 1.

1.3 Give the degeneracy of Ψ_{S,M_S} in terms of S assuming that spin-orbit coupling (see Sect. 2.1) can be neglected.

Before looking in more detail to the N-electron wave functions, we will first shortly summarize the most important aspects of the spin part of a one-electron wave function. We will follow the common practice to use lower case symbols when dealing with one-particle wave functions and uppercase for many-particle systems.

The one-electron spin functions to be considered have the quantum numbers $s = \frac{1}{2}$ and $m_s = \pm\frac{1}{2}$ and can be written in different formats:

$$|s, m_s\rangle = [|{}^1\!/_2\,, {}^1\!/_2\rangle, |{}^1\!/_2\,, -{}^1\!/_2\rangle] = [\alpha, \beta] = [\uparrow, \downarrow] \tag{1.14}$$

where [...] denotes the set of functions. When the spatial part of the wave function is explicitly written, a similar notation can be used for spin orbitals:

$$|s, m_s\rangle = \left[\varphi_1, \overline{\varphi}_2\right] \tag{1.15}$$

where the barred orbital carries the electron with $m_s = -{}^1\!/_2$. The notations by α, β and $\varphi_1, \overline{\varphi}_2$ are most frequently used and will also be followed here. The corresponding eigenvalues of the total spin operator $\hat{s}^2$ and the z-component of it ($\hat{s}_z$) are

$$\hat{s}^2\alpha = {}^1\!/_2\ ({}^1\!/_2 + 1)\,\alpha = {}^3\!/_4\,\alpha \qquad \hat{s}_z\alpha = {}^1\!/_2\,\alpha \tag{1.16a}$$

$$\hat{s}^2\beta = -{}^1\!/_2\ (-{}^1\!/_2 + 1)\,\beta = {}^3\!/_4\,\beta \qquad \hat{s}_z\beta = -{}^1\!/_2\,\beta \tag{1.16b}$$

The ladder operators $\hat{s}^{\pm} = \hat{s}_x \pm i\hat{s}_y$ change the m_s quantum number of the spin functions by the following action

$$\hat{s}^+|s, m_s\rangle = \sqrt{s(s+1) - m_s(m_s+1)}|s, m_s + 1\rangle \tag{1.17}$$

$$\hat{s}^-|s, m_s\rangle = \sqrt{s(s+1) - m_s(m_s-1)}|s, m_s - 1\rangle$$

This leads to the following simple relations when applied to the one-electron spin functions α and β:

$$\hat{s}^+\alpha = 0 \qquad \hat{s}^-\alpha = \beta \tag{1.18a}$$

$$\hat{s}^+\beta = \alpha \qquad \hat{s}^-\beta = 0 \tag{1.18b}$$

The substitution of $\hat{s}_x = \frac{1}{2}(\hat{s}^+ + \hat{s}^-)$ and $\hat{s}_y = \frac{1}{2i}(\hat{s}^+ - \hat{s}^-)$ in the expression of the total spin operator $\hat{s}^2 = \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2$ gives a simple working equation to evaluate the expectation value of $\hat{s}^2$ for spin functions:

$$\hat{s}^2 = \hat{s}^+\hat{s}^- - \hat{s}_z + \hat{s}_z^2 \tag{1.19}$$

For completeness, we also give the results of operating with $\hat{s}_x$ and $\hat{s}_y$ on α and β

$$\hat{s}_x\alpha = \frac{1}{2}\beta \qquad \hat{s}_y\alpha = -\frac{1}{2i}\beta \tag{1.20a}$$

$$\hat{s}_x\beta = \frac{1}{2}\alpha \qquad \hat{s}_y\beta = \frac{1}{2i}\alpha \tag{1.20b}$$

1.4 (a) Demonstrate that the normalization factor is one for the application of $\hat{s}^+$ to β and zero for α. (b) Derive the expression of the total spin operator $\hat{s}^2$ in terms of $\hat{s}^+$, $\hat{s}^-$ and $\hat{s}_z$. Remember that $[\hat{s}^+, \hat{s}^-] = 2\hat{s}_z$. (c) Calculate the expectation value of $\hat{s}^2$ of α and β using Eq. 1.19.

In the case of N-electron systems, the spin operators have to be applied on Slater determinants or linear combinations of these. The action of the N-electron operator $\hat{S}^2$ is most conveniently evaluated in the N-electron version of Eq. 1.19 with $\hat{S}_z$, $\hat{S}^+$ and $\hat{S}^-$ defined as the sum of the corresponding one-electron operators.

$$\hat{S}^2 = \hat{S}^+\hat{S}^- - \hat{S}_z + \hat{S}_z^2 \tag{1.21}$$

with

$$\hat{S}_z = \sum_{i=1}^{N} \hat{s}_z(i) \qquad \hat{S}^+ = \sum_{i=1}^{N} \hat{s}^+(i) \qquad \hat{S}^- = \sum_{i=1}^{N} \hat{s}^-(i) \tag{1.22}$$

The multi-electron version of Eq. 1.17 is

$$\begin{aligned} \hat{S}^+|S, M_S\rangle &= \sqrt{S(S+1) - M_S(M_S+1)}|S, M_S+1\rangle \\ \hat{S}^-|S, M_S\rangle &= \sqrt{S(S+1) - M_S(M_S-1)}|S, M_S-1\rangle \end{aligned} \tag{1.23}$$

whereas many-electron functions consisting of one Slater determinant are always eigenfunctions of $\hat{S}_z$ with an eigenvalue given by the difference of the number of α and β electrons multiplied by one half, this is in general not the case for $\hat{S}^2$. To illustrate this, we apply the two operators on the Slater determinants $|\varphi_1\varphi_2|$ and $|\varphi_1\overline{\varphi}_2|$.

$$\begin{aligned} \hat{S}_z|\varphi_1\varphi_2| &= \hat{S}_z\frac{(\varphi_1\varphi_2 - \varphi_2\varphi_1)}{\sqrt{2}} = \frac{\varphi_1\varphi_2 - \varphi_2\varphi_1}{\sqrt{2}}(\hat{s}_z(1) + \hat{s}_z(2))\alpha\alpha \\ &= \frac{\varphi_1\varphi_2 - \varphi_2\varphi_1}{\sqrt{2}}\left(\frac{1}{2}\alpha\alpha + \frac{1}{2}\alpha\alpha\right) = 1 \cdot \frac{\varphi_1\varphi_2 - \varphi_2\varphi_1}{\sqrt{2}} = 1 \cdot |\varphi_1\varphi_2| \end{aligned} \tag{1.24}$$

$$\begin{aligned} \hat{S}_z|\varphi_1\overline{\varphi}_2| &= \hat{S}_z\frac{(\varphi_1\overline{\varphi}_2 - \overline{\varphi}_2\varphi_1)}{\sqrt{2}} \\ &= \frac{\varphi_1\varphi_2(\hat{s}_z(1) + \hat{s}_z(2))\alpha\beta - \varphi_2\varphi_1(\hat{s}_z(1) + \hat{s}_z(2))\beta\alpha}{\sqrt{2}} \\ &= \frac{\varphi_1\varphi_2(1/2\,\alpha\beta - 1/2\,\alpha\beta) - \varphi_2\varphi_1(-1/2\,\beta\alpha + 1/2\,\beta\alpha)}{\sqrt{2}} \\ &= 0 \cdot \frac{\varphi_1\overline{\varphi}_2 - \overline{\varphi}_2\varphi_1}{\sqrt{2}} = 0 \cdot |\varphi_1\overline{\varphi}_2| \end{aligned} \tag{1.25}$$

This shows that the Slater determinants are eigenfunctions of $\hat{S}_z$ and the corresponding eigenvalues M_S are equal to 1 and 0, respectively. The result of applying $\hat{S}^2$ is rather straightforward using Eq. 1.21 with the notion that $(-\hat{S}_z + \hat{S}_z^2)$ gives zero when applied on the spin functions $\alpha\alpha$, $\alpha\beta$ and $\beta\alpha$. Only remains to determine the action of the two ladder operators to check whether the determinants are eigenfunctions of $\hat{S}^2$

$$\begin{aligned}
\hat{S}^+\hat{S}^-|\varphi_1\varphi_2| &= \frac{\varphi_1\varphi_2 - \varphi_2\varphi_1}{\sqrt{2}}(\hat{s}^+(1) + \hat{s}^+(2))(\hat{s}^-(1) + \hat{s}^-(2))(\alpha\alpha) \\
&= \frac{\varphi_1\varphi_2 - \varphi_2\varphi_1}{\sqrt{2}}(\hat{s}^+(1) + \hat{s}^+(2))(\beta\alpha + \alpha\beta) \\
&= \frac{\varphi_1\varphi_2 - \varphi_2\varphi_1}{\sqrt{2}}(\alpha\alpha + \alpha\alpha) = 2 \cdot \frac{\varphi_1\varphi_2 - \varphi_2\varphi_1}{\sqrt{2}} = 2|\varphi_1\varphi_2| \qquad (1.26)
\end{aligned}$$

$$\begin{aligned}
\hat{S}^+\hat{S}^-|\varphi_1\overline{\varphi}_2| &= \frac{\varphi_1\varphi_2}{\sqrt{2}}(\hat{s}^+(1) + \hat{s}^+(2))(\hat{s}^-(1) + \hat{s}^-(2))(\alpha\beta) \\
&\quad - \frac{\varphi_2\varphi_1}{\sqrt{2}}(\hat{s}^+(1) + \hat{s}^+(2))(\hat{s}^-(1) + \hat{s}^-(2))(\beta\alpha) \\
&= \frac{\varphi_1\varphi_2}{\sqrt{2}}(\hat{s}^+(1) + \hat{s}^+(2))(\beta\beta) - \frac{\varphi_2\varphi_1}{\sqrt{2}}(\hat{s}^+(1) + \hat{s}^+(2))(\beta\beta) \\
&= \frac{\varphi_1\varphi_2}{\sqrt{2}}(\alpha\beta + \beta\alpha) - \frac{\varphi_2\varphi_1}{\sqrt{2}}(\alpha\beta + \beta\alpha) = |\varphi_1\overline{\varphi}_2| + |\overline{\varphi}_1\varphi_2| \\
&\neq S(S+1)|\varphi_1\overline{\varphi}_2| \qquad (1.27)
\end{aligned}$$

Hence, the single Slater determinant $|\varphi_1\varphi_2|$ is a proper spin eigenfunction, while $|\varphi_1\overline{\varphi}_2|$ is not. In general, linear combinations of Slater determinants are necessary to ensure that the wave function is an eigenfunction of $\hat{S}^2$.

In the following, three strategies will be illustrated to construct spin eigenfunctions from scratch based on (i) projection techniques to eliminate the contributions of unwanted spin eigenfunctions, (ii) diagonalization of the matrix representation of $\hat{S}^2$, and (iii) the genealogical construction of spin functions in which spins are added one-by-one.

In the above demonstrations we have first developed the Slater determinants and then applied the spin operators. This strategy becomes of course very laborious for functions with more than two electrons. It should however be noted that it is not necessary to work with the fully expanded determinants, one gets the same results when working with the product of the diagonal elements.

1.5 Apply the total spin operator on $\Phi_1 = |\varphi_1\overline{\varphi}_1|$ and $\Phi_2 = \{|\varphi_1\overline{\varphi}_2| + |\overline{\varphi}_1\varphi_2|\}/\sqrt{2}$ and check that the same result is obtained when the determinants are fully expanded.

1.2.1 Many Electron Spin Functions by Projection

In general the spin eigenfunction of a $2S + 1$ spin multiplet is a linear combination of N-electron Slater determinants that all have the same M_S quantum number

$$^{2S+1}\Psi = \sum_L c_L \Phi_L \tag{1.28}$$

with $\hat{S}_z\Phi_L = M_S\Phi_L$ for all L. If $\{\Psi_i\}$ is a complete set of M eigenfunctions of $\hat{S}^2$ with the same M_S, *i.e.* $\hat{S}^2\Psi_i = S_i(S_i + 1)\Psi_i$ and $\hat{S}_z\Psi_i = M_S\Psi_i$ for $i = 1, M$, then any of the determinants Φ_L can be written as a linear combination of these spin eigenfunctions. In other words, any determinant Φ_L can be seen as a linear combination of different spin eigenfunctions Ψ_i and to obtain the expression of a proper spin eigenfunction one should eliminate all the undesired terms from the sum. A natural way to proceed is to apply projection techniques. Since the spin eigenvalue of Ψ_i is equal to $S_i(S_i + 1)$, the operator

$$\hat{P}^e_L = \left[\hat{S}^2 - S_L(S_L + 1)\right] \tag{1.29}$$

eliminates the L-component from the determinant Φ. Hence the subsequent application of $\hat{P}^e_i$, $\hat{P}^e_j$, $\ldots$ $\hat{P}^e_M$ (except $\hat{P}^e_k$) preserves the k-component and leads to $^{2S_k+1}\Psi_k$. This procedure is illustrated in Fig. 1.1 for a trivial example of a vector with two components. After projecting the vector on the x-axis, one subtracts this projection from the total vector to obtain the y-component.

The general expression of the operator to obtain spin eigenfunction Ψ_k from a determinant Φ_L is

$$\hat{P}_k = \prod_{l \neq k}^{M} \hat{P}^e_l = \prod_{l \neq k}^{M} \left[\hat{S}^2 - S_l(S_l + 1)\right] \tag{1.30}$$

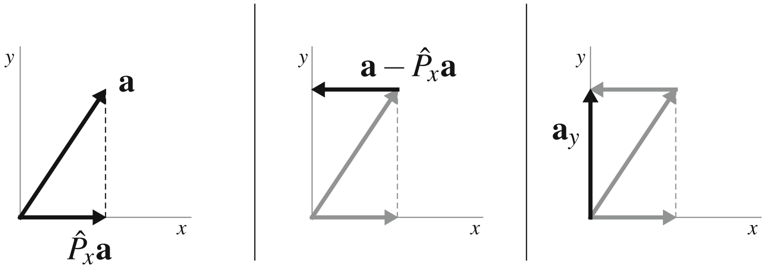


Fig. 1.1 Illustration of the projection method to eliminate undesired components of a vector. *Left* **a** is projected on the x-axis; *Middle* the projection ($\hat{P}_x$**a**) is subtracted from **a**; *Right* The result of the operation is the y-component of **a**

These expressions produce projections that are not necessarily normalized to one, but this can easily be done at the end of the process. The procedure is most conveniently illustrated by deriving the singlet and triplet open-shell spin eigenfunctions with $M_S = 0$ for a two-electron in two-orbitals case. In the notation of Eq. 1.15 the two determinants are

$$\begin{aligned} \Phi_1 &= |\varphi_1\overline{\varphi}_1\varphi_2\overline{\varphi}_2\ldots\varphi_a\overline{\varphi}_b| = |a\overline{b}| \\ \Phi_2 &= |\varphi_1\overline{\varphi}_1\varphi_2\overline{\varphi}_2\ldots\overline{\varphi}_a\varphi_b| = |\overline{a}b| \end{aligned} \tag{1.31}$$

There are two possible spin eigenfunctions, singlet and triplet, with S equal to 0 and 1, respectively. The projection operators are directly obtained from Eq. 1.30

$$\hat{P}_0 = \hat{S}^2 - 2 \qquad \hat{P}_1 = \hat{S}^2 - 0 \tag{1.32}$$

The result of applying $\hat{S}^2$ on Φ_1 is given in Eq. 1.27, and hence, the projection operators give

$$\hat{P}_0|a\overline{b}| = (\hat{S}^2 - 2)|a\overline{b}| = |a\overline{b}| + |\overline{a}b| - 2|a\overline{b}| = |\overline{a}b| - |a\overline{b}| \tag{1.33a}$$

$$\hat{P}_1|a\overline{b}| = (\hat{S}^2 - 0)|a\overline{b}| = |a\overline{b}| + |\overline{a}b| \tag{1.33b}$$

The functions have to be multiplied by $\frac{1}{\sqrt{2}}$ to obtain the properly normalized expressions.

1.6 (a) Find the other two components of the triplet spin eigenfunctions by applying the ladder operators on the $M_S = 0$ component of the triplet function. (b) Derive the singlet and triplet spin eigenfunctions by projection using Φ_2 of Eq. 1.31.

1.2.2 Spin Functions by Diagonalization

One way to find the eigenvalues and eigenvectors of an operator is to diagonalize the matrix representation of the operator in a complete basis. Therefore, a natural alternative to the projection method is the process of diagonalizing the matrix representation of the $\hat{S}^2$ operator. The basis of the matrix representation is formed by the individual determinants. The resulting eigenvectors are the spin eigenfunctions (linear combinations of these basis functions, the determinants) and the corresponding eigenvalues indicate the spin of the eigenfunction. The method is straightforward in its application but can require a substantial amount of analytical work since all matrix elements of $\hat{S}^2$ are needed, which can become rather cumbersome for systems with an elevated number of unpaired electrons. The method is illustrated for a system with three electrons in three distinct orbitals. The basis set spanned in the $M_S = \frac{1}{2}$ space contains three determinants

$$\Phi_1 = |ab\bar{c}| \qquad \Phi_2 = |a\bar{b}c| \qquad \Phi_3 = |\bar{a}bc| \tag{1.34}$$

The matrix representation of $\hat{S}^2$ can be constructed by analyzing the effect of $\hat{S}^+\hat{S}^-$, $\hat{S}_z$ and $\hat{S}_z^2$ (cf. Eq. 1.21) on the three basis functions.

$$\hat{S}^+\hat{S}^-|ab\bar{c}| = \hat{S}^+\left(|\bar{a}b\bar{c}| + |a\bar{b}\bar{c}| + 0\right) = |ab\bar{c}| + |\bar{a}bc| + |ab\bar{c}| + |a\bar{b}c| \tag{1.35a}$$

$$\hat{S}_z|ab\bar{c}| = \left(\frac{1}{2} + \frac{1}{2} - \frac{1}{2}\right)|ab\bar{c}| = \frac{1}{2}|ab\bar{c}| \tag{1.35b}$$

$$\hat{S}_z^2|ab\bar{c}| = \frac{1}{4}|ab\bar{c}| \tag{1.35c}$$

The other two determinants give analogous results and from this we evaluate the action of $\hat{S}^2$ on the three basis functions:

$$\hat{S}^2|ab\bar{c}| = {}^7\!/_4\,|ab\bar{c}| + |a\bar{b}c| + |\bar{a}bc| \tag{1.36a}$$

$$\hat{S}^2|a\bar{b}c| = |ab\bar{c}| + {}^7\!/_4\,|a\bar{b}c| + |\bar{a}bc| \tag{1.36b}$$

$$\hat{S}^2|\bar{a}bc| = |ab\bar{c}| + |a\bar{b}c| + {}^7\!/_4\,|\bar{a}bc| \tag{1.36c}$$

which leads to the following matrix representation of $\hat{S}^2$

$$\begin{array}{c|ccc} & |ab\bar{c}\rangle & |a\bar{b}c\rangle & |\bar{a}bc\rangle \\ \hline \langle ab\bar{c}| & \frac{7}{4} & 1 & 1 \\ \langle a\bar{b}c| & 1 & \frac{7}{4} & 1 \\ \langle \bar{a}bc| & 1 & 1 & \frac{7}{4} \end{array} \tag{1.37}$$

As can be seen, the matrix has non-zero off diagonal matrix elements showing that the basis set of determinants is not a basis of eigenfunctions of the $\hat{S}^2$ operator. From here, the search for spin eigenfunctions follows standard diagonalization schemes. First, the eigenvalues are determined by finding the x-values for which the secular determinant is zero

$$\begin{vmatrix} \frac{7}{4} - x & 1 & 1 \\ 1 & \frac{7}{4} - x & 1 \\ 1 & 1 & \frac{7}{4} - x \end{vmatrix} = 0 \tag{1.38}$$

This gives $x_1, x_2 = \frac{3}{4}$ and $x_3 = \frac{15}{4}$, corresponding to two doublet functions $(\frac{1}{2}(\frac{1}{2} + 1) = \frac{3}{4})$ and one quartet function $(\frac{3}{2}(\frac{3}{2} + 1) = \frac{15}{4})$. The corresponding eigenvectors are determined by substituting the respective x-values in the secular equations.

$$\begin{pmatrix} \frac{7}{4} & 1 & 1 \\ 1 & \frac{7}{4} & 1 \\ 1 & 1 & \frac{7}{4} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = x \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} \tag{1.39}$$

This gives $c_1 = c_2 = c_3 = \frac{1}{\sqrt{3}}$ for $x = \frac{15}{4}$, where the normalization condition is used to determine the numerical value. The quartet spin function with $M_S = \frac{1}{2}$ is given by

$$^4\Psi = \frac{1}{\sqrt{3}} \left(|ab\bar{c}| + |a\bar{b}c| + |\bar{a}bc| \right) \tag{1.40}$$

1.7 Find the $M_S = -\frac{1}{2}, \pm\frac{3}{2}$ components of the quartet function with the ladder operators.

The situation for the doublet functions is more complicated. The resulting equations for the coefficients are linear dependent ($c_2 + c_3 = -c_1$; $c_1 + c_3 = -c_2$; $c_1 + c_2 = -c_3$) and no unique solution can be determined. This is expected since the two functions have the same eigenvalues of $\hat{S}^2$ and any linear combination of the two doublet functions is also an eigenfunction. In some cases the spatial symmetry of the system imposes extra restrictions on the coefficients such that a unique solution emerges. For instance, in a system with inversion symmetry and center b located on the inversion center, c_1 must be equal to $\pm c_3$ and the following two doublet functions fulfil spatial and spin symmetry conditions.

$$^2\Psi_A = \frac{1}{\sqrt{2}} \left(|ab\bar{c}| - |\bar{a}bc| \right) \tag{1.41a}$$

$$^2\Psi_B = \frac{1}{\sqrt{6}} \left(2|a\bar{b}c| - |ab\bar{c}| - |\bar{a}bc| \right) \tag{1.41b}$$

1.8 (a) Check that the two doublets are orthogonal. (b) Check that the expectation value of $\hat{S}^2$ for $^2\Psi_A$ is 3/4.

1.2.3 Genealogical Approach

The third method to obtain spin eigenfunctions is based on a stepwise generation of the N-electron spin eigenfunction through a one-by-one addition of one-electron spin functions to a known spin eigenfunction. This genealogical way of constructing

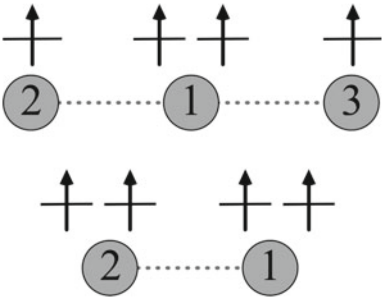


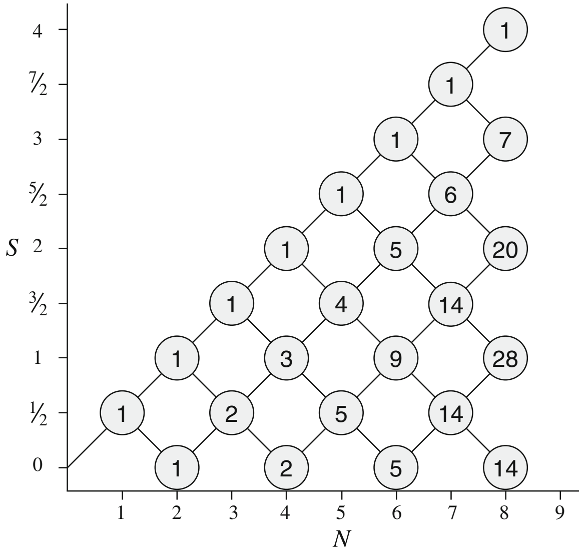
Fig. 1.2 Model system with four unpaired electrons on three centers (*top*). The two electrons on center 1 are coupled to a triplet state as stated by Hund's rule. Singlet coupling on center 1 leads to states that are much higher in energy and not directly relevant for the magnetic interactions. The *lower part* shows the system with four electrons on two centers

spin eigenfunctions is described in great detail by Pauncz [1, 2] and we refer to these books for further reading. Here, we will describe the main characteristics of the method and illustrate it with a system with four unpaired electrons localized on two or three magnetic centers as shown in Fig. 1.2.

The starting point of the method is the one electron spin function α with $S = \frac{1}{2}$ to which a second electron spin can be *added* to give an $S = 1$ spin function or *subtracted*, resulting in an $S = 0$ function. Subsequently more electron spins can be added or subtracted until the desired number of spins are described in the spin eigenfunctions. The use of Clebsch–Gordon coefficients ensures that linear combinations of determinants are produced that are eigenfunctions of $\hat{S}^2$ at each stage of the procedure. An advantage of this method is that one can specifically construct a certain spin eigenfunction among all possible with the required spin couplings between the electrons. This is best illustrated in the branching diagram shown in Fig. 1.3, which represents the different routes that can be taken to construct a spin function with a given S-value (on the y-axis) for a certain number of electrons (on the x-axis). The way up along the branching diagram represents *adding* an electron spin (increasing S by $\frac{1}{2}$) and going downwards indicates that an electron spin is *subtracted*, that is, S is diminished from S to $S - \frac{1}{2}$. The number in the circles gives the number of different routes that can be taken to arrive at that point. For instance, there are two ways to construct a singlet spin function with four electrons, three different triplet functions and one quintet. The branching diagrams allows us to choose one specific path to reach the desired spin function. This can be very useful, for example, to impose high spin coupling between unpaired electrons on the same magnetic center to fulfill Hund's rule.

The formulas for adding and subtracting an electron spin look somewhat awkward but are rather simple in their application. Moreover, the method is very well suited for translation into a computer program. *Adding* a spin is done with

Fig. 1.3 Branching diagram



$$\Psi(N, S, M_S) = \Big[(S + M_S)^{\frac{1}{2}}\Psi(N-1, S-\frac{1}{2}, M_S-\frac{1}{2})\alpha(N) + (S - M_S)^{\frac{1}{2}}\Psi(N-1, S-\frac{1}{2}, M_S+\frac{1}{2})\beta(N)\Big] \times (2S)^{-\frac{1}{2}} \tag{1.42}$$

and the *subtraction* of a spin requires

$$\Psi(N, S, M_S) = \Big[-(S - M_S + 1)^{\frac{1}{2}}\Psi(N-1, S+\frac{1}{2}, M_S-\frac{1}{2})\alpha(N) + (S + M_S + 1)^{\frac{1}{2}}\Psi(N-1, S+\frac{1}{2}, M_S+\frac{1}{2})\beta(N)\Big] \times (2S+2)^{-\frac{1}{2}} \tag{1.43}$$

The first example that will be discussed concerns the generation of the spin eigenfunctions relevant for the magnetic interactions in a system with three magnetic centers and four unpaired electrons, see Fig. 1.2 (top). Two of these four electrons are localized on the same center and coupled to a local triplet state. Hund's rule tells us that the singlet coupling of these two electrons gives rise to an electronic configuration that is much higher in energy and not directly relevant for the magnetic interactions as will be discussed in Chap. 2. Starting by assigning α to electron 1, the pathway marked in the first diagram of Fig. 1.4 shows that adding a second electron spin provides us the required triplet spin eigenfunction for the two electrons on the

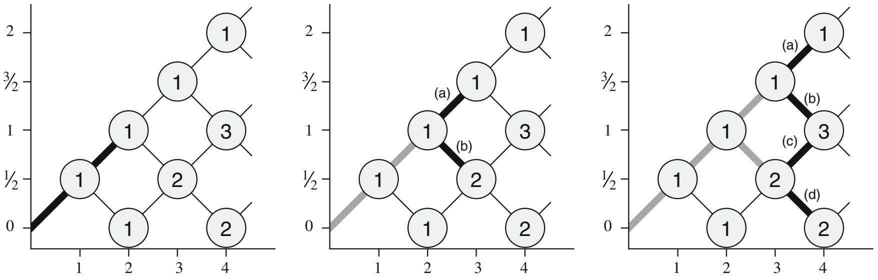


Fig. 1.4 Paths to generate spin eigenfunctions with 2 (*left*), 3 (*middle*) and 4 (*right*) electrons under the restriction of triplet coupling of electrons 1 and 2

same magnetic center. The *downwards* path leads to singlet coupling and is ruled out for this example. Equation 1.42 is applied with $N = 2$, $S = 1$ and $M_S = 1$.

$$\Psi(2, 1, 1) = \left[(1+1)^{\frac{1}{2}}\alpha(1)\alpha(2) + (1-1)^{\frac{1}{2}} \cdot 0 \cdot \beta(2)\right](2 \cdot 1)^{-\frac{1}{2}} = \alpha\alpha \tag{1.44}$$

The third electron spin, localized on the second magnetic center can be coupled parallel or anti-parallel to this triplet, giving a quartet ($S = \frac{3}{2}$) or doublet ($S = \frac{1}{2}$) function, as shown in the middle diagram of Fig. 1.4. The quartet function is obtained from Eq. 1.42 with $N = 3$, $S = \frac{3}{2}$ and $M_S = \frac{3}{2}$.

$$\begin{aligned}\Psi(3, {}^3\!/_2, {}^3\!/_2) = &\left[({}^3\!/_2 + {}^3\!/_2)^{1/2}\, \alpha(1)\alpha(2)\alpha(3) + ({}^3\!/_2 - {}^3\!/_2)^{1/2} \cdot 0 \cdot \beta(3)\right] \\ &\times (2 \cdot {}^3\!/_2)^{-\frac{1}{2}} = \alpha\alpha\alpha\end{aligned} \tag{1.45}$$

On the other hand, the doublet spin function is generated with Eq. 1.43 with $N = 3$, $S = \frac{1}{2}$ and $M_S = \frac{1}{2}$; and $\Psi(N-1, S + {}^1\!/_2, M_S - {}^1\!/_2)$ is obtained by applying the $\hat{S}^-$ operator to $\Psi(2, 1, 1)$ given in Eq. 1.44:

$$\begin{aligned}\Psi(3, {}^1\!/_2, {}^1\!/_2) = &\left[-({}^1\!/_2 - {}^1\!/_2 + 1)^{1/2}\, \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]\alpha(3)\right. \\ &\left. + \ ({}^1\!/_2 + {}^1\!/_2 + 1)^{1/2}\, \alpha(1)\alpha(2)\beta(3)\right](2 \cdot {}^1\!/_2 + 2)^{-1/2} \\ = &\frac{1}{\sqrt{6}}(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha)\end{aligned} \tag{1.46}$$

The incorporation of the fourth electron spin can be done in four different ways. $\Psi(3, {}^3\!/_2, {}^3\!/_2)$ creates a quintet and a triplet state, while $\Psi(3, {}^1\!/_2, {}^1\!/_2)$ leads to a second triplet and a singlet state, as illustrated in the right diagram of Fig. 1.4.

$$\begin{aligned}\Psi(4,2,2) &= \left[(2+2)^{\frac{1}{2}}\alpha(1)\alpha(2)\alpha(3)\alpha(4) + (2-2)^{\frac{1}{2}}\cdot 0\cdot \beta(4)\right](2\cdot 2)^{-\frac{1}{2}}\\ &= \alpha\alpha\alpha\alpha \qquad (1.47)\end{aligned}$$

To generate the triplet function by subtraction, we need the expression of $\Psi(3, {}^{3}\!/_{2}, {}^{1}\!/_{2})$, which can be obtained by operating on $\Psi(3, {}^{3}\!/_{2}, {}^{3}\!/_{2})$ with the $\hat{S}^{-}$ operator.

$$\begin{aligned}\Psi(4,1,1) = \Big[&-(2-2+1)^{\frac{1}{2}}\frac{1}{\sqrt{3}}\,[\beta(1)\alpha(2)\alpha(3)+\alpha(1)\beta(2)\alpha(3)\\ &+\ \alpha(1)\alpha(2)\beta(3)]\,\alpha(4) + (1+1+1)^{\frac{1}{2}}\alpha(1)\alpha(2)\alpha(3)\beta(4)\Big](2\cdot 1+2)^{-\frac{1}{2}}\\ =\ &\frac{1}{2\sqrt{3}}(3\alpha\alpha\alpha\beta - \beta\alpha\alpha\alpha - \alpha\beta\alpha\alpha - \alpha\alpha\beta\alpha) \qquad (1.48)\end{aligned}$$

The generation of the second triplet function from the doublet state by addition gives

$$\begin{aligned}\Psi'(4,1,1) = \Big[&(1+1)^{\frac{1}{2}}\frac{1}{\sqrt{6}}[2\alpha(1)\alpha(2)\beta(3) - \alpha(1)\beta(2)\alpha(3)\\ &-\beta(1)\alpha(2)\alpha(3)]\alpha(4) + (1-1)^{\frac{1}{2}}\cdot 0\cdot\beta(4)\Big](2\cdot 1)^{-\frac{1}{2}}\\ =\ &\frac{1}{\sqrt{6}}(2\alpha\alpha\beta\alpha - \alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha) \qquad (1.49)\end{aligned}$$

Note that $\Psi(4, 1, 1)$ and $\Psi'(4, 1, 1)$ are degenerate with respect to the $\hat{S}^2$ operator, and therefore any linear combination of these two functions is equally valid. In analogy to the discussion for the doublet states in the previous section, the spatial symmetry can impose extra conditions on the values of the coefficients of the determinants. If the second and third magnetic center are symmetry equivalent, the interchange of the coordinates of electron 3 and 4 should leave the wave function unaltered, except for a possible sign change. This is obviously not the case for the here generated spin functions, but the linear combinations $\Psi(4, 1, 1) + \frac{2}{\sqrt{2}}\Psi'(4, 1, 1)$ and $\Psi(4, 1, 1) - \frac{1}{\sqrt{2}}\Psi'(4, 1, 1)$ give

$$\begin{aligned}\widetilde{\Psi}(4,1,1) &= \frac{1}{\sqrt{2}}(\alpha\alpha\alpha\beta - \alpha\alpha\beta\alpha)\\ &= \frac{1}{\sqrt{2}}\,[\alpha\alpha(\alpha\beta - \beta\alpha)] \qquad (1.50a)\\ \widetilde{\Psi}'(4,1,1) &= \frac{1}{2}(\alpha\alpha\alpha\beta + \alpha\alpha\beta\alpha - \alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha)\\ &= \frac{1}{2}\,[\alpha\alpha(\alpha\beta + \beta\alpha) - (\alpha\beta + \beta\alpha)\alpha\alpha] \qquad (1.50b)\end{aligned}$$

which are (anti-)symmetric under the permutation of electron 3 and 4. Furthermore, these two linear combinations clearly reveal the triplet coupling of electron 1 and 2, and the singlet ($\widetilde{\Psi}$) or triplet coupling ($\widetilde{\Psi}'$) for electron 3 and 4.

Remains to evaluate the function generated by the incorporation of the fourth electron spin by subtraction from the three-electron doublet function. This gives a singlet spin function characterized by the triplet coupling of electron 1 and 2 (following Hund's rule) and of electron 3 and 4. To apply Eq. 1.43, the $\Psi(3, \frac{1}{2}, -\frac{1}{2})$ function has to be generated by acting with $\hat{S}^-$ on $\Psi(3, \frac{1}{2}, \frac{1}{2})$.

$$\begin{aligned}
\Psi(4, 0, 0) = \Big[&- (0 - 0 + 1)^{\frac{1}{2}} \frac{1}{\sqrt{6}}[-2\beta(1)\beta(2)\alpha(3) + \beta(1)\alpha(2)\beta(3) \\
&+ \alpha(1)\beta(2)\beta(3)]\alpha(4) + (0 + 0 + 1)^{\frac{1}{2}} \frac{1}{\sqrt{6}}[2\alpha(1)\alpha(2)\beta(3) \\
&- \alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3)]\beta(4)\Big](2 \cdot 0 + 2)^{-\frac{1}{2}} \\
= &\frac{1}{2\sqrt{3}}[2(\alpha\alpha\beta\beta + \beta\beta\alpha\alpha) - \alpha\beta\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta - \beta\alpha\beta\alpha] \\
= &\frac{1}{2\sqrt{3}}[2(\alpha\alpha\beta\beta + \beta\beta\alpha\alpha) - (\alpha\beta + \beta\alpha)(\alpha\beta + \beta\alpha)]
\end{aligned} \tag{1.51}$$

1.9 (a) Construct a branching diagram and mark the path to generate the $N = 4$ triplet and singlet spin states with singlet coupling for electron 1 and 2. (b) Construct $\Psi(2, 0, 0)$ with the genealogical approach.

Two-by-two additions: The process of generating spin functions by the genealogical approach can be made a little less tedious by considering the incorporation of two electrons at the same time. An additional advantage of doing so is that one better controls the spin coupling of electron pairs. The triplet functions with four electrons, $\Psi(4, 1, 1)$ and $\Psi'(4, 1, 1)$ Eqs. 1.48 and 1.49 do have triplet coupling among electron 1 and 2, but turn out to be mixtures of singlet and triplet coupling for electrons 3 and 4. Only after taking the correct linear combination, spin functions could be constructed with clear-cut spin couplings of both electron pairs. This can be achieved directly with the Serber variant of the genealogical approach [3, 4] illustrated in the branching diagram of Fig. 1.5.

Starting with an $N-2$-electron spin function of spin S', singlet or triplet coupled two-electron functions are added to obtain $\Psi(N, S)$ with $S = S'+1$, S' or $S'-1$. The branching diagram shows that four different cases can be distinguished, for which the following formulas need to be considered:

- case 1: Singlet incorporation (gray solid lines); $S = S'$

$$\Psi(N, S, M_S) = \Psi(N-2, S, M_S)\Phi_a \tag{1.52}$$

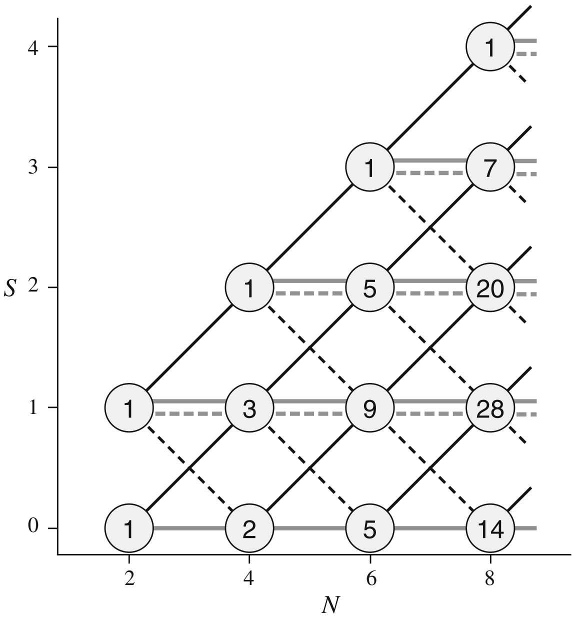


Fig. 1.5 Branching diagram for two-by-two electron incorporations. *Gray* solid lines represent singlet coupled additions. The other lines represent triplet additions with $S = S' - 1$ (*black dashed*), $S = S'$ (*gray dashed*) and $S = S' + 1$ (*black solid*)

- case 2: Triplet incorporation (black solid lines); $S = S' + 1$

$$\begin{aligned}\Psi(N, S, M_S) = \Big[&\{(S + M_S)(S + M_S - 1)\}^{\frac{1}{2}} \Psi(N - 2, S - 1, M_S - 1)\Phi_b \\ &+ \{2(S + M_S)(S - M_S)\}^{\frac{1}{2}} \Psi(N - 2, S - 1, M_S)\Phi_c \\ &+ \{(S - M_S)(S - M_S - 1)\}^{\frac{1}{2}} \Psi(N - 2, S - 1, M_S + 1)\Phi_d \Big] \\ &\times [2S(2S - 1)]^{-\frac{1}{2}}\end{aligned} \tag{1.53}$$

- case 3: Triplet incorporation (gray dashed lines); $S = S'$

$$\begin{aligned}\Psi(N, S, M_S) = \Big[&-\{(S + M_S)(S - M_S + 1)\}^{\frac{1}{2}} \Psi(N - 2, S, M_S - 1)\Phi_b \\ &+ \sqrt{2} M_S \Psi(N - 2, S, M_S)\Phi_c \\ &+ \{(S - M_S)(S + M_S + 1)\}^{\frac{1}{2}} \Psi(N - 2, S, M_S + 1)\Phi_d \Big] \\ &\times [2S(S + 1)]^{-\frac{1}{2}}\end{aligned} \tag{1.54}$$

- case 4: Triplet incorporation (black dashed lines): $S = S' - 1$

$$\begin{aligned}\Psi(N,S,M_S) = \Big[&\{(S-M_S+2)(S-M_S+1)\}^{\frac{1}{2}}\Psi(N-2,S+1,M_S-1)\Phi_b \\ &- \{2(S-M_S+1)(S+M_S+1)\}^{\frac{1}{2}}\Psi(N-2,S+1,M_S)\Phi_c \\ &+ \{(S+M_S+1)(S+M_S+2)\}^{\frac{1}{2}}\Psi(N-2,S+1,M_S+1)\Phi_d\Big] \\ &\times [(2S+2)(2S+3)]^{-\frac{1}{2}} \end{aligned} \tag{1.55}$$

with

$$\Phi_a = \frac{1}{\sqrt{2}}[\alpha(N-1)\beta(N) - \beta(N-1)\alpha(N)] \tag{1.56a}$$

$$\Phi_b = \alpha(N-1)\alpha(N) \tag{1.56b}$$

$$\Phi_c = \frac{1}{\sqrt{2}}[\alpha(N-1)\beta(N) + \beta(N-1)\alpha(N)] \tag{1.56c}$$

$$\Phi_d = \beta(N-1)\beta(N) \tag{1.56d}$$

The method is nicely illustrated for a system with two magnetic centers, both with two unpaired electrons as shown in Fig. 1.2 (bottom). Hund's rule dictates that the electrons on each magnetic center are preferably coupled to a local triplet. Hence, the starting point in the Serber diagram is $\Psi(2,1,1) = \alpha(1)\alpha(2)$ and depending on the route taken one obtains a quintet (black), a triplet (gray dashed) or a singlet (black dashed) state. Equations 1.53 and 1.55 lead to the same expressions for the quintet as singlet state as with the standard genealogical approach. In contrast, the triplet state obtained from Eq. 1.54 is directly the correct expression and not a linear combination of singlet and triplet coupling among electron 3 and 4 as before (see Eqs. 1.48–1.50).

$$\begin{aligned}\Psi(4,1,0) = \Big[&-\{(1+0)(1-0+1)\}^{\frac{1}{2}}\beta(1)\beta(2)\alpha(3)\alpha(4) \\ &+ \sqrt{2}\cdot 0\cdot\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)+\beta(1)\alpha(2)]\frac{1}{\sqrt{2}}[\alpha(3)\beta(4)+\beta(3)\alpha(4)] \\ &+ \{(1+0)(1+0+1)\}^{\frac{1}{2}}\alpha(1)\alpha(2)\beta(3)\beta(4)\Big]\{2\cdot 1(1+1)\}^{-\frac{1}{2}} \\ = &\frac{1}{\sqrt{2}}[\alpha\alpha\beta\beta - \beta\beta\alpha\alpha] \end{aligned} \tag{1.57}$$

1.10 (a) Check that the expressions in Eqs. 1.50b and 1.57 are two different M_S components of the same triplet. (b) Construct $\Psi(4,1,0)$ with singlet coupling of electron 1 and 2 and triplet coupling for 3 and 4. Use the Serber variant of the genealogical approach.

1.2.4 Final Remarks

The examples given in the precedent paragraphs cover many real-world cases. The two-electrons in two-orbitals case discussed in Sect. 1.2.1 is representative of all types of Cu^{II} binuclear complexes or organic biradicals. It is important to remind that the intuitive representation with an up and down spin often used to indicate the open-shell singlet state in these cases (see Fig. 1.6) is not the most rigorous representation of this quantum state and may lead to confusion. It corresponds to the $|\alpha(1)\beta(2)|$ determinant and is actually a mixture of the $M_S = 0$ components of singlet and triplet functions.

Similar considerations hold for the three unpaired electrons case of Sect. 1.2.2. While the three parallel electrons on the transition metal centers on the left side of Fig. 1.7 give a satisfactory representation of the high-spin situation, i.e. the quartet

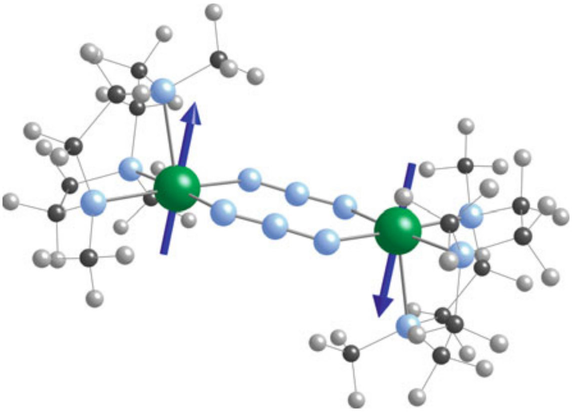


Fig. 1.6 Ball and stick representation of a $Cu_2(\mu\text{-}N_3)_2$ complex. The arrows on the Cu^{II} ions (*green*) are indications of the spin moment of the unpaired electron in the Cu-3d orbitals

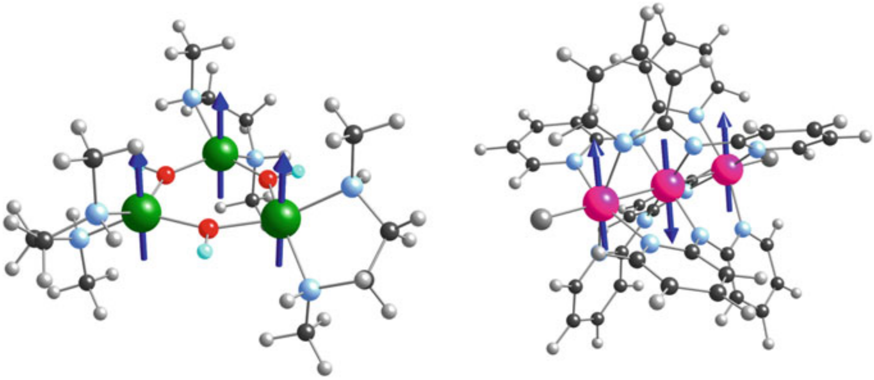


Fig. 1.7 Ball and stick representation of a $Cu_3(OH)_3$ complex (*left*) and an extended metal atom chain (EMAC) made of three Cr^{2+} ions hold together by four tridentate organic ligands

state, the up-down-up situation depicted on the right is not the doublet state but rather a superposition of the doublet and quartet spin functions given in Eqs. 1.40 and 1.41.

1.11 Calculate the overlap of the quartet and doublet spin functions given in Eqs. 1.40 and 1.41 with the $|\alpha\beta\alpha|$ determinant.

1.3 Perturbation Theory

Many body perturbation theory is one of the fundamental tools in Quantum Chemistry. It takes a central place both in the calculation of accurate energies and wave functions, and in the analysis of results for reaching a better understanding of the sometimes complicated physics contained in the system. There are basically two flavors of many-body perturbation theory. The first is what one calls the diagonalize-and-then-perturb method, and the second one inverts this order, it follows a perturb-and-then-diagonalize approach.

When one is only interested in a single state that is well separated from all the others, for example a non-degenerate ground state, the distinction is not very relevant. Using a proper zeroth-order wave function such as the one provided by the Hartree–Fock approach, the effect of electron correlation can be estimated with any standard perturbation scheme, being the Møller–Plesset implementation the most common one.

However, it becomes a little more subtle when one wants to describe a collection of states of a quantum system that are close in energy, or when states with a marked multiconfigurational character have to be described. The reference space is now spanned by several Slater determinants that define a collection of electronic states. Most approaches first diagonalize the reference space and then introduce the effect of the external determinants with perturbation theory. In contrast, quasi-degenerate perturbation theory (QDPT), first addresses the external determinants for all the matrix elements among the reference determinants and then diagonalizes the reference space to obtain the energies and wave functions of the states of interest.

1.3.1 Rayleigh–Schrödinger Perturbation Theory

There are only few systems for which the Schrödinger equation can be solved exactly. Therefore, many schemes have been developed to obtain as accurate as possible approximate solutions. The perturbative treatment is based on the partition of the full Hamiltonian of the system in two parts.

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{V} \tag{1.58}$$

The first term is the Hamiltonian of a model system with a complete set of known (normalized) solutions

$$\hat{H}^{(0)}\psi_i^{(0)} = E_i^{(0)}\psi_i^{(0)} \tag{1.59}$$

and $\hat{V}$ is the perturbation operator, which *perturbs* the model system. The parameter λ can be varied from zero (no perturbation) to one (complete Hamiltonian). In addition to this splitting of the Hamiltonian, the energy and the wave function are expanded in Taylor series writing the exact solutions as the sum of the model system solutions and corrections in the first, second, third, and higher order of the perturbation

$$\begin{aligned} \psi_0 &= \psi_0^{(0)} + \lambda\psi_0^{(1)} + \lambda^2\psi_0^{(2)} + \lambda^3\psi_0^{(3)} + \cdots \\ E_0 &= E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \lambda^3 E_0^{(3)} + \cdots \end{aligned} \tag{1.60}$$

where the subscript “0” makes reference to the ground state. The substitution of Eqs. 1.58 and 1.60 in the Schrödinger equation of the full system leads to

$$\begin{aligned} &(\hat{H}^{(0)} + \lambda\hat{V})\left(\psi_0^{(0)} + \lambda\psi_0^{(1)} + \lambda^2\psi_0^{(2)} + \cdots\right) \\ &\quad = \left(E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \cdots\right)\left(\psi_0^{(0)} + \lambda\psi_0^{(1)} + \lambda^2\psi_0^{(2)} + \cdots\right) \end{aligned} \tag{1.61}$$

Since λ can in principle take any value between 0 and 1, this equation only has a solution when the sum of the left-hand terms of a certain power of λ are equal to the sum of the right-hand terms of the same power of λ. This permits us to split the equation and group the terms by the power of λ

$$\lambda^0 : \quad \hat{H}^{(0)}\psi_0^{(0)} = E_0^{(0)}\psi_0^{(0)} \tag{1.62a}$$

$$\lambda^1 : \quad \hat{H}^{(0)}\psi_0^{(1)} + \hat{V}\psi_0^{(0)} = E_0^{(0)}\psi_0^{(1)} + E_0^{(1)}\psi_0^{(0)} \tag{1.62b}$$

$$\lambda^2 : \quad \hat{H}^{(0)}\psi_0^{(2)} + \hat{V}\psi_0^{(1)} = E_0^{(0)}\psi_0^{(2)} + E_0^{(1)}\psi_0^{(1)} + E_0^{(2)}\psi_0^{(0)} \tag{1.62c}$$

1.12 Write down the equation for the terms that are cubic in λ.

These equations can now be solved one-by-one to determine the different corrections to $E^{(0)}$and $\psi^{(0)}$ in order to approximate the solutions of the full system. The equation that stems from the terms that are independent of λ defines the model system and does not provide new information. The first-order correction to the energy ($E_0^{(1)}$) can be determined from the equation with the linear λ terms. For that purpose we first multiply all terms with $\psi_0^{(0)*}$ and then integrate over the electron coordinates.

$$\langle\psi_0^{(0)}|\hat{H}^{(0)}|\psi_0^{(1)}\rangle + \langle\psi_0^{(0)}|\hat{V}|\psi_0^{(0)}\rangle = E_0^{(0)}\langle\psi_0^{(0)}|\psi_0^{(1)}\rangle + E_0^{(1)}\langle\psi_0^{(0)}|\psi_0^{(0)}\rangle \tag{1.63}$$

Since the zeroth-order wave function of the ground state is normalized, this equation can be rewritten to

$$E_0^{(1)} = \langle\psi_0^{(0)}|\hat{H}^{(0)}|\psi_0^{(1)}\rangle + \langle\psi_0^{(0)}|\hat{V}|\psi_0^{(0)}\rangle - E_0^{(0)}\langle\psi_0^{(0)}|\psi_0^{(1)}\rangle \tag{1.64}$$

The only unknown quantity on the right-hand-side of this equation is $\psi_0^{(1)}$. Therefore it is expanded as a linear combination of excited state wave functions of the unperturbed system.

$$\psi_0^{(1)} = \sum_{i\neq 0} a_i \psi_i^{(0)} \tag{1.65}$$

These wave functions of the excited states of the model system are all known and together with $\psi_0^{(0)}$ they form a complete set of functions. The orthogonality to $\psi_0^{(0)}$ is ensured by excluding this term from the linear combination. The substitution of the expansion in Eq. 1.64 leads to

$$E_0^{(1)} = \sum_{i\neq 0}\langle\psi_0^{(0)}|\hat{H}^{(0)}|\psi_i^{(0)}\rangle + \langle\psi_0^{(0)}|\hat{V}|\psi_0^{(0)}\rangle - \sum_{i\neq 0} E_0^{(0)}\langle\psi_0^{(0)}|\psi_i^{(0)}\rangle \tag{1.66}$$

By realizing that $\hat{H}^{(0)}|\psi_i^{(0)}\rangle = E_i^{(0)}|\psi_i^{(0)}\rangle$, the orthogonality of the different eigenfunctions of the zeroth-order model makes that all right-hand-side terms are zero, except the second one. Hence, the first-order correction to the energy is

$$E_0^{(1)} = \langle\psi_0^{(0)}|\hat{V}|\psi_0^{(0)}\rangle, \tag{1.67}$$

which corresponds to the expectation value of the perturbation operator for the unperturbed wave function. To determine the first-order corrected wave function, we need to find the values of the expansion coefficients a_i of Eq. 1.65. This can be done by substituting the expansion in the equation linear in λ Eq. 1.62b and after multiplying by $\psi_k^{(0)*}$ we integrate over the electron coordinates

$$\begin{aligned}&\sum_{i\neq 0} a_i\langle\psi_k^{(0)}|\hat{H}^{(0)}|\psi_i^{(0)}\rangle + \langle\psi_k^{(0)}|\hat{V}|\psi_0^{(0)}\rangle\\ &= \sum_{i\neq 0} a_i\langle\psi_k^{(0)}|\psi_i^{(0)}\rangle E_0^{(0)} + \langle\psi_k^{(0)}|\psi_0^{(0)}\rangle E_0^{(1)}\end{aligned} \tag{1.68}$$

Taking into account the orthogonality of the zeroth-order eigenvectors, the only non-zero terms in the summation are those when $i = k$ and the equation simplifies to

$$a_k E_k^{(0)} + \langle \psi_k^{(0)} | \hat{V} | \psi_0^{(0)} \rangle = a_k E_0^{(0)} + 0 \tag{1.69}$$

from which a_k and $\psi^{(1)}$ follow immediately

$$a_k = \frac{\langle \psi_k^{(0)} | \hat{V} | \psi_0^{(0)} \rangle}{E_0^{(0)} - E_k^{(0)}} \qquad \psi^{(1)} = \sum_{i \neq 0} \frac{\langle \psi_i^{(0)} | \hat{V} | \psi_0^{(0)} \rangle}{E_0^{(0)} - E_i^{(0)}} \psi_i^{(0)} \tag{1.70}$$

The second-order correction to the energy is obtained from the quadratic equation in λ Eq. 1.62c in a similar fashion as the first-order correction. First, we multiply the equation by $\psi_0^{(0)*}$ and then we integrate over the electron coordinates

$$\begin{aligned} &\langle \psi_0^{(0)} | \hat{H}^{(0)} | \psi_0^{(2)} \rangle + \langle \psi_0^{(0)} | \hat{V} | \psi_0^{(1)} \rangle \\ &\quad = E_0^{(0)} \langle \psi_0^{(0)} | \psi_0^{(2)} \rangle + E_0^{(1)} \langle \psi_0^{(0)} | \psi_0^{(1)} \rangle + E_0^{(2)} \langle \psi_0^{(0)} | \psi_0^{(0)} \rangle \end{aligned} \tag{1.71}$$

Orthogonality causes the first and second term on the right-hand-side to be zero and the substitution of $\psi_0^{(2)}$ by a linear combination of zeroth-order eigenfunctions leads to the following equation

$$\sum_{j \neq 0} b_j \langle \psi_0^{(0)} | \hat{H}^{(0)} | \psi_j^{(0)} \rangle + \langle \psi_0^{(0)} | \hat{V} | \psi_0^{(1)} \rangle = E_0^{(2)} \tag{1.72}$$

The first left-hand-side term is zero and after substituting Eq. 1.70, the second order correction to the energy is obtained

$$E_0^{(2)} = \sum_{i \neq 0} \frac{\langle \psi_0^{(0)} | \hat{V} | \psi_i^{(0)} \rangle \langle \psi_i^{(0)} | \hat{V} | \psi_0^{(0)} \rangle}{E_0^{(0)} - E_i^{(0)}} \tag{1.73}$$

Higher order corrections can be derived in a similar way, but the expressions get more complicated rapidly.

When excited state energies of the model system ($E_i^{(0)}$) are close to $E_0^{(0)}$, the corresponding terms in the summations of $\psi^{(1)}$and $E^{(2)}$diverge, unless the matrix elements of these terms are zero. In case of a degenerate ground state of the model system, say $E_0^{(0)} = E_i^{(0)} = \cdots = E_k^{(0)}$, we can solve this problem by first diagonalizing the full $\hat{H}$ in the basis of $\psi_0^{(0)}, \psi_i^{(0)}, \ldots, \psi_k^{(0)}$. This yields linear combinations of $\psi_0^{(0)}, \psi_i^{(0)}, \ldots, \psi_k^{(0)}$ that are equally valid as zeroth-order wave functions while the divergence problem is avoided since the diagonalization process made all non-diagonal matrix elements equal to zero. Note that in case of near, but not strict degeneracy, this *diagonalize-and-then-perturb* procedure yields model wave functions that are no longer eigenfunctions of $\hat{H}^{(0)}$.

1.3.2 Møller–Plesset Perturbation Theory

As mentioned above, a common implementation of many-body perturbation theory in quantum chemistry is based on the zeroth-order Hamiltonian proposed by Møller and Plesset. When the Hartree–Fock wave function Φ_{HF} is known, the zeroth-order Hamiltonian can be defined as the sum of the Fock operators

$$\hat{H}^{(0)} = \sum_{i}^{N} \hat{f}(i) \tag{1.74}$$

with N is the number of electrons and

$$\hat{f}(i) = \hat{h}(i) + \sum_{k} \left(\hat{J}_k(i) - \hat{K}_k(i) \right) = \hat{h}(i) + \hat{g}(i) \tag{1.75}$$

The perturbation operator corresponds to the difference of the instantaneous electron–electron interaction operator and the mean-field electron–electron interaction of the Hartree–Fock description

$$\hat{V} = \hat{H} - \hat{H}^{(0)} = \sum_{i} \hat{h}(i) + \sum_{i} \sum_{j>i} \frac{1}{r_{ij}} - \sum_{i} \left(\hat{h}(i) + \hat{g}(i) \right) = \sum_{i} \sum_{j>i} \frac{1}{r_{ij}} - \sum_{i} \hat{g}(i) \tag{1.76}$$

The zeroth-order (known) solutions are defined by

$$\hat{H}^{(0)} \Psi_k^{(0)} = E_k^{(0)} \Psi_k^{(0)} \tag{1.77}$$

with

$$\Psi_0^{(0)} = \Phi_{HF} = |\phi_1 \phi_2 \ldots \phi_j \phi_k \ldots \phi_N| \qquad E_0^{(0)} = \sum_{m} \varepsilon_m \tag{1.78a}$$

$$\Psi_j^{(0)} = |\phi_1 \phi_2 \ldots \phi_k \ldots \phi_N \phi_a| = \Phi_j^a \qquad E_j^{(0)} = E_0^{(0)} - \varepsilon_j + \varepsilon_a \tag{1.78b}$$

$$\Psi_{jk}^{(0)} = |\phi_1 \phi_2 \ldots\ldots \phi_N \phi_a \phi_b| = \Phi_{jk}^{ab} \qquad E_{jk}^{(0)} = E_0^{(0)} - \varepsilon_j - \varepsilon_k + \varepsilon_a + \varepsilon_b \tag{1.78c}$$

The first order correction to the energy can be calculated with Eq. 1.67 and using the Slater–Condon rules one arrives at the following expression

$$
\begin{aligned}
E_0^{(1)} &= \langle \Psi^{(0)} | \hat{V} | \Psi^{(0)} \rangle = \langle \Phi_{HF} | \sum_i \sum_{i>j} \frac{1}{r_{ij}} | \Phi_{HF} \rangle - \langle \Phi_{HF} | - \sum_i \hat{g}(i) | \Phi_{HF} \rangle \\
&= \frac{1}{2} \sum_i \langle \phi_i | \sum_j \hat{J}_j - \hat{K}_j | \phi_i \rangle - \sum_i \langle \phi_i | \sum_j \hat{J}_j - \hat{K}_j | \phi_i \rangle \\
&= -\frac{1}{2} \sum_i \langle \phi_i | \sum_j \hat{J}_j - \hat{K}_j | \phi_i \rangle \qquad (1.79)
\end{aligned}
$$

This leads the following expression for the energy at first-order

$$
E_0 = E_0^{(0)} + E_0^{(1)} = \sum_i \varepsilon_i - \frac{1}{2} \sum_i \langle \phi_i | \sum_j \hat{J}_j - \hat{K}_j | \phi_i \rangle = E_{HF} \qquad (1.80)
$$

The first order correction to the wave function is

$$
\Psi_0^{(1)} = \sum_{i \neq 0} \frac{\langle \Psi_i^{(0)} | \hat{V} | \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_i^{(0)}} | \Psi_i^{(0)} \rangle \qquad (1.81)
$$

The numerator can be simplified by replacing $\hat{V}$ by $\hat{H} - \hat{H}^{(0)}$

$$
\begin{aligned}
\langle \Psi_i^{(0)} | \hat{V} | \Psi_0^{(0)} \rangle &= \langle \Psi_i^{(0)} | \hat{H} | \Psi_0^{(0)} \rangle - \langle \Psi_i^{(0)} | \hat{H}^{(0)} | \Psi_0^{(0)} \rangle \\
&= \langle \Psi_i^{(0)} | \hat{H} | \Psi_0^{(0)} \rangle - E_0^{(0)} \langle \Psi_i^{(0)} | \Psi_0^{(0)} \rangle = \langle \Psi_i^{(0)} | \hat{H} | \Psi_0^{(0)} \rangle \qquad (1.82)
\end{aligned}
$$

This last term is zero for determinants that arise from single excitations Eq. 1.78b because of Brillouin's theorem. It is also zero for determinants with more than two electron replacements, and hence, only the double excitations Eq. 1.78c need to be considered. This observation also serves to simplify the second-order correction to the energy

$$
E_0^{(2)} = \sum_{i \neq 0} \frac{\langle \Psi_0^{(0)} | \hat{H} | \Psi_i^{(0)} \rangle \langle \Psi_i^{(0)} | \hat{H} | \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_i^{(0)}} = \sum_{\substack{a<b \\ i<j}} \frac{\langle \Psi_0^{(0)} | \hat{H} | \Phi_{ij}^{ab} \rangle \langle \Phi_{ij}^{ab} | \hat{H} | \Psi_0^{(0)} \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \qquad (1.83)
$$

Again, only the doubly excited determinants have to be considered to calculate the second-order correction to the energy. The expression for the third-order correction to the energy is slightly more complicated but as most salient feature introduces the effect of the interaction between excited determinants.

$$E_0^{(3)} = \sum_{\substack{a<b\\i<j}}\sum_{\substack{c<d\\k<l}} \frac{\langle \Psi_0^{(0)}|\hat{H}|\Phi_{ij}^{ab}\rangle\langle \Phi_{ij}^{ab}|\hat{H}|\Phi_{kl}^{cd}\rangle\langle \Phi_{kl}^{cd}|\hat{H}|\Psi_0^{(0)}\rangle}{(\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b)(\varepsilon_k+\varepsilon_l-\varepsilon_c-\varepsilon_d)} - E_0^{(1)}\sum_{\substack{a<b\\i<j}} \frac{|\langle \Psi_0^{(0)}|\hat{H}|\Phi_{ij}^{ab}\rangle|^2}{(\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b)^2} \tag{1.84}$$

1.3.3 Quasi-Degenerate Perturbation Theory

The second-order correction to the energy given in Eq. 1.83 diverges when the denominator goes to zero, that is when the zeroth-order energy of excited Slater determinants becomes close to $E^{(0)}$. Moreover, in such situations one is usually interested not only in the lowest state, but in a number of low-lying *nearly-degenerate* states. In such cases one should go beyond the single determinant description of the zeroth-order problem and extend the reference with other low-energy determinants.

Let $\mathbb{S}$ be the collection of Slater determinants that span the Hilbert space of the full Hamiltonian of a system. The complete space is divided in a model space $\mathbb{S}_0$ and an external space $\mathbb{S}'$.

$$\mathbb{S} = \mathbb{S}_0 + \mathbb{S}' \tag{1.85}$$

with $\mathbb{S}_0 = \{\Phi_I, \Phi_J, \ldots\}$ and $\mathbb{S}' = \{\Phi_R, \Phi_S, \ldots\}$. The model space contains all the determinants that significantly contribute to the (multiconfigurational) wave functions of the lowest, nearly degenerate electronic states. In ordinary many-body perturbation theory, one would first diagonalize the full Hamiltonian in the subspace $\mathbb{S}_0$ to construct the reference wave functions $\Psi^{(0)}$ and then include the effect of the determinants of $\mathbb{S}'$ through the expressions of the second- (or higher-) order perturbation theory in a state-by-state manner as schematically illustrated in Fig. 1.8. This is the *diagonalize-and-then-perturb* approach. On the contrary, quasi-degenerate perturbation theory first takes into account the effect of the external determinants on the interactions among the determinants of $\mathbb{S}_0$ and then diagonalizes the resulting matrix to obtain the N-electron wave functions and energies of the states of interest. This modification of the matrix elements of $\mathbb{S}_0$ is often called *dressing* or *screening* and leads to an effective Hamiltonian that not only describes the bare coupling between the determinants of the model space, but also the effects of electron correlation. The expression for the effective Hamiltonian at the second-order of perturbation is

$$\langle \Phi_I|\hat{H}^{\mathit{eff}}|\Phi_J\rangle = \langle \Phi_I|\hat{H}|\Phi_J\rangle + \sum_{R\in\mathbb{S}'} \frac{\langle \Phi_I|\hat{H}|\Phi_R\rangle\langle \Phi_R|\hat{H}|\Phi_J\rangle}{E_J^{(0)} - E_R^{(0)}} \tag{1.86}$$

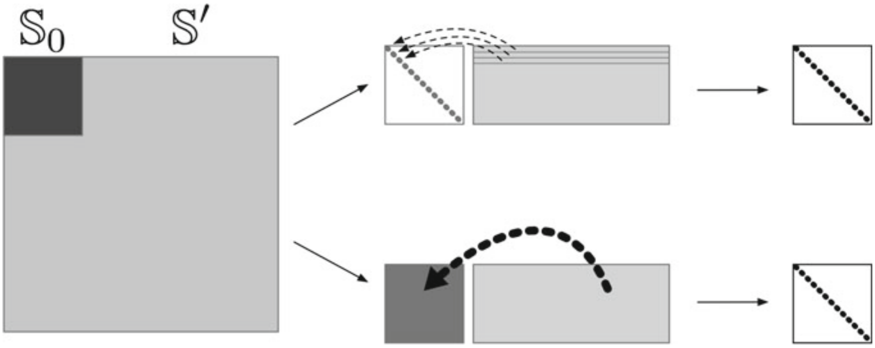


Fig. 1.8 Schematic representation of the diagonalize-then-perturb approach (*top*) and perturb-then-diagonalize (*bottom*) approaches. In the upper scheme, the model space is diagonalized and then the effect of the external determinants is included state-by-state. In the lower scheme, all matrix elements of the model space are perturbed and subsequently the model space is diagonalized

It is obvious from the denominator in the second term that the matrix will become non-Hermitian when the zeroth-order energies of the determinants in $\mathbb{S}_0$ are not the same. Therefore, this recipe only works for (nearly-)degenerate states. One advantage of this '*perturb-and-then-diagonalize*' approach is that the length of the wave function expansion remains of the dimension of the model space, and hence, especially suitable for analysis purposes. Multideterminantal perturbation schemes that follow the '*diagonalize-and-then-perturb*' approach are described in Sect. 4.3.3.

1.4 Effective Hamiltonian Theory

The exact N-electron wave function can be thought of to be an infinite linear combination of Slater determinants built from an infinitely large orbital set. While such a wave function is only a hypothetical object, lengthy wave function expansions can be considered to be good approximations to the exact solution. Hence, they will provide us with accurate energies and other observables of the system that can be extracted from the wave function by calculating the expectation value of the corresponding operator. However, such lengthy wave functions are often not easily *understood* and the extraction of simple models with predictive and interpretative power is not straightforward. Ideally, one would like to have a compact wave function with only a small number of Slater determinants, without loosing the accuracy of the nearly exact wave function.

Effective Hamiltonian theory establishes a connection between accuracy and interpretation. It is used in many fields of chemistry and physics in different variants and sometimes confused with model Hamiltonians. In the scope of this monograph, the latter term is used for simple Hamiltonians that find their origin in physical/chemical intuition, and hence, are phenomenological in nature. These model Hamiltonians have been put forward to interpret experimental measurements and capture the complex physics of a system in simpler concepts. The parameters of the model are usually determined by fitting the experimental data to analytical expressions derived from the model Hamiltonian.

In the significance used here the effective Hamiltonian maps a lengthy, highly-accurate wave function onto a much smaller subspace in such a way that the diagonalization of the subspace gives exactly the same eigenvalues as those of the nearly exact wave functions and the corresponding eigenvectors are projections of the original wave functions. The dimension of the subspace is typically the same as the dimension of the space spanned by some widely used model Hamiltonian. In this way, a one-to-one correspondence can be established between the *ab initio* calculations and the model Hamiltonian. Hence, the effective Hamiltonian theory provides a rigorous procedure to extract model parameters from accurate calculations.

Similar to what is done in QDPT, a model space $\mathbb{S}_0$ of dimension N is defined as a subspace of the full Hilbert space $\mathbb{S}$ of dimension M. Remember that QDPT is used to determine accurate wave functions and energies starting from a limited description of the system based on the model space. However, in the present case, the accurate energies and wave functions are already known and the action goes in the opposite direction; the lengthy wave function of length M is mapped on the smaller subspace $\mathbb{S}_0$ ensuring a minimum loss of the information contained in the full solution.

In the first place, the eigenfunctions of $\mathbb{S}$ (Ψ_k) have to be projected onto the model space by applying the projection operator

$$\hat{P}_{\mathbb{S}_0} = \sum_{i=1}^{N} |\Phi_i\rangle\langle\Phi_i| \tag{1.87}$$

where Φ_i is the basis of the model space. Among the projected vectors $\widetilde{\Psi}_k = \hat{P}_{\mathbb{S}_0}\Psi_k$, the N projections are selected that have the largest norm. These vectors are often defined as the basis of the so-called target space $\mathbb{S}_T$ and are used to construct the effective Hamiltonian. However, the vectors $\widetilde{\Psi}_k$ are in general not orthogonal. In the original formulation of Bloch [5] the projections are transformed to their biorthogonal form by

$$\widetilde{\Psi}_k^{\dagger} = S^{-1}\widetilde{\Psi}_k \tag{1.88}$$

with

$$\langle\widetilde{\Psi}_k|\widetilde{\Psi}_l^{\dagger}\rangle = \langle\widetilde{\Psi}_k^{\dagger}|\widetilde{\Psi}_l\rangle = \delta_{kl} \qquad \langle\widetilde{\Psi}_k|\widetilde{\Psi}_l\rangle = \langle\widetilde{\Psi}_k^{\dagger}|\widetilde{\Psi}_l^{\dagger}\rangle = S_{kl} \tag{1.89}$$

The effective Hamiltonian can now be expressed in its spectral decomposition

$$\hat{H}^{\mathit{eff}} = \sum_{k\in\mathbb{S}_T} |\widetilde{\Psi}_k\rangle E_k \langle\widetilde{\Psi}_k^{\dagger}| \tag{1.90}$$

However, this definition leads to a non-Hermitian Hamiltonian, which may not be the most optimal representation for interpretation. Therefore, one often adopts the orthogonalization of the projections proposed by des Cloizeaux, which involves the $S^{-1/2}$ overlap matrix [6]:

$$\widetilde{\Psi}_k^{\perp} = S^{-1/2}\,\widetilde{\Psi}_k \tag{1.91}$$

This procedure produces orthogonal vectors and all elements of the target space are affected in a similar degree. The effective Hamiltonian constructed with these vectors is hermitian and reads

$$\hat{H}^{eff} = \sum_{k \in \mathbb{S}_T} |\widetilde{\Psi}_k^{\perp}\rangle E_k \langle \widetilde{\Psi}_k^{\perp}| \tag{1.92}$$

The third possibility for processing the projected vectors is the Gram-Schmidt orthogonalization, in which the projections are sequentially orthogonalized. Starting with the normalization of $\widetilde{\Psi}_1$, the second vector is orthogonalized by projecting out the component of vector 1. Then $\widetilde{\Psi}_3$ is orthogonalized on $\widetilde{\Psi}_1$ and $\widetilde{\Psi}_2$, and so on. This means that the first vectors in the process are only slightly affected by the orthogonalization, while the last one is completely determined by the orthogonality condition. This loss of information—the coefficients of the projection of the last vector are not used—may be advantageous when some roots, i.e. computed (approximate) wavefunctions, in the target space are (nearly) degenerate with other roots in the external space. In such cases, the norm of the projection may be rather small and the information hold in the projections is not always well-founded, since strong mixing may have occurred with the states that are in the external space. The energy of these states can be considered as reliable, mixing among (nearly) degenerate states does not affect the energy.

In short, an effective Hamiltonian can be constructed from the following recipe.

- Choose a relevant model space of dimension N and write down the Slater determinants that constitute the basis of this space. It may be handy to work out all the matrix elements of the model Hamiltonian.
- Select the N eigenfunctions of the full Hilbert space (e.g. obtained in an *ab initio* calculation) with the largest projection onto the model space. (Bi-)orthonormalize the projections of these vectors and take the total energy of one of the roots as zero of energy.
- Calculate the matrix elements $\langle \Phi_I | \hat{H}^{eff} | \Phi_J \rangle$ of the effective Hamiltonian using the definition given in Eq. 1.90 or Eq. 1.92. One can check the procedure by diagonalizing the resulting matrix. This should give the same energies as found in the *ab initio* calculation and the corresponding eigenvectors have to be identical to the projections of these roots.

When the effective Hamiltonian is constructed from *ab initio* wave functions the resulting matrix is numerical in nature. This matrix can be used to determine the values of the parameters of a phenomenological model Hamiltonian, but also to check the validity of the model. In most cases the structure of the effective Hamiltonian matrix coincides with the structure of the model Hamiltonian, but when significant deviations are observed, it should not be discarded that important interactions are missing in the model. For instance, when non-zero matrix elements appear in the effective Hamiltonian at places where the model Hamiltonian is zero, one should revise the expression of the model Hamiltonian. This brings us to the second type of effective Hamiltonians that falls under the scope of this monograph; the analytical effective Hamiltonian. The above sketched procedure to derive a numerical Hamiltonian can also be used to map the analytical expressions of a precise, but complicated model Hamiltonian onto a simpler one. In this way one can rigorously derive new model Hamiltonians, for example when the comparison between a numerical effective Hamiltonian and a simple model Hamiltonian fails.

Problems

1.1 Ordering by spatial or spin part. In the notation of multideterminantal wave functions, one can either respect as much as possible the order of the spatial part in the different determinants, or strictly maintain the order of the spin part. Construct singlet and triplet functions for a two-electrons in two-orbitals case respecting (i) the order of the spatial part and (ii) the order of the spin part of the total wave function.

1.2 Coulomb, exchange or other. Classify the following two-electron integrals as Coulomb, exchange or other integral and assign a relative size (*large*, *medium*, or *small* to the integrals:

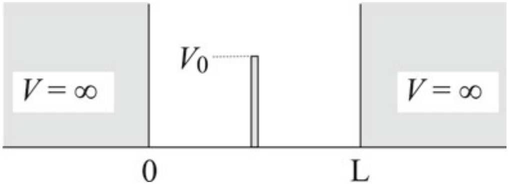
(a) $\langle\phi_a(1)\phi_b(2)|\frac{1}{r_{12}}|\phi_a(1)\phi_b(2)\rangle$ (b) $\int\frac{\phi_a(1)\phi_b(1)\phi_a(2)\phi_b(2)}{r_{12}}d\tau_1 d\tau_2$

(c) $\langle\phi_a(1)\overline{\phi}_c(2)|\frac{1-\hat{P}_{12}}{r_{12}}|\phi_c(1)\overline{\phi}_a(2)\rangle$ (d) $\langle\phi_b(1)\phi_c(2)|\frac{1}{r_{12}}|\phi_c(1)\phi_d(2)\rangle$

(e) $\int\phi_a(1)\phi_c(2)\frac{1}{r_{12}}\phi_c(1)\phi_a(2)d\tau_1 d\tau_2$ (f)$\langle\phi_b(1)\phi_d(2)|\frac{\hat{P}_{12}}{r_{12}}|\phi_d(1)\phi_b(2)\rangle$

ϕ_a and ϕ_b are centered on site A, ϕ_c and ϕ_d on site B.

1.3 Perturbation theory. The prototype *particle in a box* problem is perturbed by a finite potential V_0 of width γ centered at $x=\frac{1}{2}L$. Calculate the first-order energy correction for the ground state, and the first and second excited states.



Reminder: $\psi_n^{(0)}(x)=\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$ and $E_n^{(0)}=\frac{hn^2}{8mL^2}$, Assume that γ is small enough to consider $\psi^{(0)}$constant in the $\frac{1}{2}L-\frac{1}{2}\gamma\ldots\frac{1}{2}L+\frac{1}{2}\gamma$ interval.

1.4 Effective Hamiltonians: The following (hypothetical) model Hamiltonian is used to analyze a certain experimental observation

	$\lvert\Phi_1\rangle$	$\lvert\Phi_2\rangle$	$\lvert\Phi_3\rangle$
$\langle\Phi_1\rvert$	0		
$\langle\Phi_2\rvert$	μ	Δ_1	
$\langle\Phi_3\rvert$	γ	$(\gamma - 4\mu)/2$	Δ_2

To get insight in the parameters of the model Hamiltonian an *ab initio* calculation was performed giving the following multideterminantal wave functions Ψ_k and energies E_k.

	Ψ_1	Ψ_2	Ψ_3	Ψ_4	Ψ_5
Φ_1	0.4804	0.8486	−0.0381	−0.2147	0.0387
Φ_2	0.3203	0.3990	−0.1391	−0.7732	0.3480
Φ_3	0.1601	0.0495	0.9468	0.0437	0.2714
Φ_4	0.8006	0.3397	−0.1109	0.4293	−0.2167
Φ_5	0.0000	0.0526	−0.2656	0.4122	0.8699
E	−0.50	−0.38	−0.40	−0.36	−0.20

a. Determine the norm of the projections of Ψ_k on the model space.
b. Select the three roots with the largest norm and orthogonalize the projections $\widetilde{\Psi}_k$
c. Construct the 3 × 3 effective Hamiltonian and diagonalize the resulting matrix. Are the eigenvalues of $\hat{H}^{eff}$ equal to the eigenvalues of Ψ_k?
d. Determine the value of the model parameters. Is the model Hamiltonian consistent with the *ab initio* result?

References

1. R. Pauncz, *Spin Eigenfunctions* (Plenum Press, New York, 1979)
2. R. Pauncz, *The Construction of Spin Eigenfunctions: An Exercise Book* (Kluwer Academic/Plenum Publishers, New York, 2000)
3. R. Serber, Phys. Rev. **45**, 461 (1934)
4. R. Serber, J. Chem. Phys. **2**, 697 (1934)
5. C. Bloch, Nucl. Phys. **6**, 329 (1958)
6. J. des Cloizeaux, Nucl. Phys. **20**, 321 (1960)