

Chapter 11

One Must be Able to Evaluate the Matrix Elements Among Properly Symmetry Adapted N-Electron Configuration Functions for Any Operator, the Electronic Hamiltonian in Particular. The Slater-Condon Rules Provide this Capability

I. CSFs Are Used to Express the Full N-Electron Wavefunction

It has been demonstrated that a given electronic configuration can yield several space- and spin- adapted determinantal wavefunctions; such functions are referred to as configuration state functions (CSFs). These CSF wavefunctions are not the exact eigenfunctions of the many-electron Hamiltonian, H ; they are simply functions which possess the space, spin, and permutational symmetry of the exact eigenstates. As such, they comprise an acceptable set of functions to use in, for example, a linear variational treatment of the true states.

In such variational treatments of electronic structure, the N-electron wavefunction is expanded as a sum over all CSFs that possess the desired spatial and spin symmetry:

$$\Psi = \sum_J C_J \Phi_J.$$

Here, the Φ_J represent the CSFs that are of the correct symmetry, and the C_J are their expansion coefficients to be determined in the variational calculation. If the spin-orbitals used to form the determinants, that in turn form the CSFs $\{\Phi_J\}$, are orthonormal one-electron functions (i.e., $\langle \phi_k | \phi_j \rangle = \delta_{k,j}$), then the CSFs can be shown to be orthonormal functions of N electrons

$$\langle \Phi_J | \Phi_K \rangle = \delta_{J,K}.$$

In fact, the Slater determinants themselves also are orthonormal functions of N electrons whenever orthonormal spin-orbitals are used to form the determinants.

The above expansion of the full N-electron wavefunction is termed a "configuration-interaction" (CI) expansion. It is, in principle, a mathematically rigorous approach to expressing Ψ because the set of all determinants that can be formed from a complete set of spin-orbitals can be shown to be complete. In practice, one is limited to the number of orbitals that can be used and in the number of CSFs that can be included in the CI expansion. Nevertheless, the CI expansion method forms the basis of the most commonly used techniques in quantum chemistry.

In general, the optimal variational (or perturbative) wavefunction for any (i.e., the ground or excited) state will include contributions from spin-and space-symmetry adapted determinants derived from all possible configurations. For example, although the determinant with $L = 1, S = 1, M_L = 1, M_S = 1$ arising from the $1s^2 2s^2 2p^2$ configuration may contribute strongly to the true ground electronic state of the Carbon atom, there will be contributions from all configurations which can provide these $L, S, M_L,$ and M_S values (e.g., the $1s^2 2s^2 2p^1 3p^1$ and $2s^2 2p^4$ configurations will also contribute, although the $1s^2 2s^2 2p^1 3s^1$ and $1s^2 2s^1 2p^2 3p^1$ will not because the latter two configurations are odd under inversion symmetry whereas the state under study is even).

The mixing of CSFs from many configurations to produce an optimal description of the true electronic states is referred to as configuration interaction (CI). Strong CI (i.e., mixing of CSFs with large amplitudes appearing for more than one dominant CSF) can occur, for example, when two CSFs from different electronic configurations have nearly the same Hamiltonian expectation value. For example, the $1s^2 2s^2$ and $1s^2 2p^2 \ ^1S$ configurations of Be and the analogous ns^2 and np^2 configurations of all alkaline earth atoms are close in energy because the ns - np orbital energy splitting is small for these elements; the σ^2 and π^2 configurations of ethylene become equal in energy, and thus undergo strong CI mixing, as the CC bond is twisted by 90° in which case the σ and π^* orbitals become degenerate.

Within a variational treatment, the relative contributions of the spin-and space-symmetry adapted CSFs are determined by solving a secular problem for the eigenvalues (E_i) and eigenvectors (C_i) of the matrix representation H of the full many-electron Hamiltonian \mathbf{H} within this CSF basis:

$$\sum_L H_{K,L} C_{i,L} = E_i C_{i,K}.$$

The eigenvalue E_i gives the variational estimate for the energy of the i^{th} state, and the entries in the corresponding eigenvector $C_{i,K}$ give the contribution of the K^{th} CSF to the i^{th} wavefunction ψ_i in the sense that

$$\psi_i = \sum_K C_{i,K} \psi_K,$$

where ψ_K is the K^{th} CSF.

II. The Slater-Condon Rules Give Expressions for the Operator Matrix Elements Among the CSFs

To form the $H_{K,L}$ matrix, one uses the so-called Slater-Condon rules which express all non-vanishing determinantal matrix elements involving either one- or two- electron operators (one-electron operators are additive and appear as

$$F = \sum_i f(i);$$

two-electron operators are pairwise additive and appear as

$$G = \sum_{ij} g(i,j).$$

Because the CSFs are simple linear combinations of determinants with coefficients determined by space and spin symmetry, the $H_{I,J}$ matrix in terms of determinants can be used to generate the $H_{K,L}$ matrix over CSFs.

The Slater-Condon rules give the matrix elements between two determinants

$$|> = | 1 2 3 \dots N |$$

and

$$| '> = | '1 '2 '3 \dots 'N |$$

for any quantum mechanical operator that is a sum of one- and two- electron operators ($F + G$). It expresses these matrix elements in terms of one- and two-electron integrals involving the spin-orbitals that appear in $|>$ and $| '>$ and the operators f and g .

As a first step in applying these rules, one must examine $|>$ and $| '>$ and determine by how many (if any) spin-orbitals $|>$ and $| '>$ differ. In so doing, one may have to reorder the spin-orbitals in one of the determinants to achieve maximal coincidence with those in the other determinant; it is essential to keep track of the number of permutations (N_p) that one makes in achieving maximal coincidence. The results of the Slater-Condon rules given below are then multiplied by $(-1)^{N_p}$ to obtain the matrix elements between the original $|>$ and $| '>$. The final result does not depend on whether one chooses to permute $|>$ or $| '>$.

Once maximal coincidence has been achieved, the Slater-Condon (SC) rules provide the following prescriptions for evaluating the matrix elements of any operator $F + G$ containing a one-electron part $F = \sum_i f(i)$ and a two-electron part $G = \sum_{ij} g(i,j)$ (the Hamiltonian is, of course, a specific example of such an operator; the electric dipole

operator $\sum_i e \mathbf{r}_i$ and the electronic kinetic energy $-\hbar^2/2m_e \sum_i \nabla_i^2$ are examples of one-electron operators (for which one takes $g = 0$); the electron-electron coulomb interaction $\sum_{i>j} e^2/r_{ij}$ is a two-electron operator (for which one takes $f = 0$):

The Slater-Condon Rules

(i) If $|\psi\rangle$ and $|\psi'\rangle$ are identical, then

$$\langle \psi | F + G | \psi \rangle = \sum_i \langle \psi | f | \psi \rangle + \sum_{i>j} [\langle \psi | g | \psi \rangle - \langle \psi | g | \psi \rangle],$$

where the sums over i and j run over all spin-orbitals in $|\psi\rangle$;

(ii) If $|\psi\rangle$ and $|\psi'\rangle$ differ by a single spin-orbital mismatch ($p \rightarrow p'$),

$$\langle \psi | F + G | \psi' \rangle = \langle p | f | p' \rangle + \sum_j [\langle p | g | p' \rangle - \langle p | g | p' \rangle],$$

where the sum over j runs over all spin-orbitals in $|\psi\rangle$ except p ;

(iii) If $|\psi\rangle$ and $|\psi'\rangle$ differ by two spin-orbitals ($p \rightarrow p'$ and $q \rightarrow q'$),

$$\langle \psi | F + G | \psi' \rangle = \langle p | g | p' \rangle \langle q | g | q' \rangle - \langle p | g | q' \rangle \langle q | g | p' \rangle$$

(note that the F contribution vanishes in this case);

(iv) If $|\psi\rangle$ and $|\psi'\rangle$ differ by three or more spin orbitals, then

$$\langle \psi | F + G | \psi' \rangle = 0;$$

(v) For the identity operator I , the matrix elements $\langle \psi | I | \psi' \rangle = 0$ if $|\psi\rangle$ and $|\psi'\rangle$ differ by one or more spin-orbitals (i.e., the Slater determinants are orthonormal if their spin-orbitals are).

Recall that each of these results is subject to multiplication by a factor of $(-1)^{N_p}$ to account for possible ordering differences in the spin-orbitals in $|\psi\rangle$ and $|\psi'\rangle$.

In these expressions,

$$\langle \psi | f | \psi \rangle$$

is used to denote the one-electron integral

$$\int \psi_i^*(r) f(r) \psi_j(r) dr$$

and

$$\langle \psi | g | \psi \rangle \text{ (or in short hand notation } \langle ij | kl \rangle)$$

represents the two-electron integral

$$\int \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}') g(\mathbf{r}, \mathbf{r}') \psi_k(\mathbf{r}) \psi_l(\mathbf{r}') d\mathbf{r} d\mathbf{r}'.$$

The notation $\langle ij | kl \rangle$ introduced above gives the two-electron integrals for the $g(\mathbf{r}, \mathbf{r}')$ operator in the so-called Dirac notation, in which the i and k indices label the spin-orbitals that refer to the coordinates \mathbf{r} and the j and l indices label the spin-orbitals referring to coordinates \mathbf{r}' . The \mathbf{r} and \mathbf{r}' denote x, y, z and x', y', z' (with α and β being the x or y spin functions). The fact that \mathbf{r} and \mathbf{r}' are integrated and hence represent 'dummy' variables introduces index permutational symmetry into this list of integrals. For example,

$$\langle ij | kl \rangle = \langle ji | lk \rangle = \langle kl | ij \rangle^* = \langle lk | ji \rangle^*;$$

the final two equivalences are results of the Hermitian nature of $g(\mathbf{r}, \mathbf{r}')$.

It is also common to represent these same two-electron integrals in a notation referred to as Mulliken notation in which:

$$\int \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}') g(\mathbf{r}, \mathbf{r}') \psi_k(\mathbf{r}) \psi_l(\mathbf{r}') d\mathbf{r} d\mathbf{r}' = (ik | jl).$$

Here, the indices i and k , which label the spin-orbital having variables \mathbf{r} are grouped together, and j and l , which label spin-orbitals referring to the \mathbf{r}' variables appear together. The above permutational symmetries, when expressed in terms of the Mulliken integral list read:

$$(ik | jl) = (jl | ik) = (ki | lj)^* = (lj | ki)^*.$$

If the operators f and g do not contain any electron spin operators, then the spin integrations implicit in these integrals (all of the ψ_i are spin-orbitals, so each ψ_i is accompanied by an α or β spin function and each ψ_i^* involves the adjoint of one of the α or β spin functions) can be carried out as $\langle \alpha | \alpha \rangle = 1$, $\langle \alpha | \beta \rangle = 0$, $\langle \beta | \alpha \rangle = 0$, $\langle \beta | \beta \rangle = 1$, thereby yielding integrals over spatial orbitals. These spin integration results follow immediately from the general properties of angular momentum eigenfunctions detailed in Appendix G; in particular, because α and β are eigenfunctions of S_z with different eigenvalues, they must be orthogonal $\langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0$.

The essential results of the Slater-Condon rules are:

1. The full $N!$ terms that arise in the N -electron Slater determinants do not have to be treated explicitly, nor do the $N!(N! + 1)/2$ Hamiltonian matrix elements among the $N!$ terms of one Slater determinant and the $N!$ terms of the same or another Slater determinant.
2. All such matrix elements, for any one- and/or two-electron operator can be expressed in terms of one- or two-electron integrals over the spin-orbitals that appear in the determinants.
3. The integrals over orbitals are three or six dimensional integrals, regardless of how many electrons N there are.
4. These integrals over mo's can, through the LCAO-MO expansion, ultimately be expressed in terms of one- and two-electron integrals over the primitive atomic orbitals. It is only these ao-based integrals that can be evaluated explicitly (on high speed computers for all but the smallest systems).

III. Examples of Applying the Slater-Condon Rules

It is wise to gain some experience using the SC rules, so let us consider a few illustrative example problems.

1. What is the contribution to the total energy of the 3P level of Carbon made by the two $2p$ orbitals alone? Of course, the two $1s$ and two $2s$ spin-orbitals contribute to the total energy, but we artificially ignore all such contributions in this example to simplify the problem.

Because all nine of the 3P states have the same energy, we can calculate the energy of any one of them; it is therefore prudent to choose an "easy" one

$$^3P(M_L=1, M_S=1) = |p_1 \ p_0 \ |.$$

The energy of this state is $\langle p_1 \ p_0 \ | H \ | p_1 \ p_0 \ \rangle$. The SC rules tell us this equals:

$$I_{2p_1} + I_{2p_0} + \langle 2p_1 2p_0 | 2p_1 2p_0 \rangle - \langle 2p_1 2p_0 | 2p_0 2p_1 \rangle,$$

where the short hand notation $I_j = \langle j | f | j \rangle$ is introduced.

If the contributions from the two $1s$ and two $2s$ spin-orbitals are now taken into account, one obtains a total energy that also contains $2I_{1s} + 2I_{2s} + \langle 1s 1s | 1s 1s \rangle + 4\langle 1s 2s | 1s 2s \rangle - 2\langle 1s 2s | 2s 1s \rangle + \langle 2s 2s | 2s 2s \rangle + 2\langle 1s 2p_1 | 1s 2p_1 \rangle - \langle 1s 2p_1 | 2p_1 1s \rangle + 2\langle 1s 2p_0 | 1s 2p_0 \rangle - \langle 1s 2p_0 | 2p_0 1s \rangle + 2\langle 2s 2p_1 | 2s 2p_1 \rangle - \langle 2s 2p_1 | 2p_1 2s \rangle + 2\langle 2s 2p_0 | 2s 2p_0 \rangle - \langle 2s 2p_0 | 2p_0 2s \rangle$.

2. Is the energy of another 3P state equal to the above state's energy? Of course, but it may prove informative to prove this.

Consider the $M_S=0, M_L=1$ state whose energy is:

$$\begin{aligned}
 & 2^{-1/2} \langle [p_1 p_0 | + | p_1 p_0 |] | H | [p_1 p_0 | + | p_1 p_0 |] \rangle 2^{-1/2} \\
 &= 1/2 \{ I_{2p_1} + I_{2p_0} + \langle 2p_1 2p_0 | 2p_1 2p_0 \rangle + I_{2p_1} + I_{2p_0} + \langle 2p_1 2p_0 | 2p_1 2p_0 \rangle \} \\
 &+ 1/2 \{ - \langle 2p_1 2p_0 | 2p_0 2p_1 \rangle - \langle 2p_1 2p_0 | 2p_0 2p_1 \rangle \} \\
 &= I_{2p_1} + I_{2p_0} + \langle 2p_1 2p_0 | 2p_1 2p_0 \rangle - \langle 2p_1 2p_0 | 2p_0 2p_1 \rangle.
 \end{aligned}$$

Which is, indeed, the same as the other 3P energy obtained above.

3. What energy would the singlet state $2^{-1/2} \langle [p_1 p_0 | - | p_1 p_0 |]$ have?

The $^3P M_S=0$ example can be used (changing the sign on the two determinants) to give

$$E = I_{2p_1} + I_{2p_0} + \langle 2p_1 2p_0 | 2p_1 2p_0 \rangle + \langle 2p_1 2p_0 | 2p_0 2p_1 \rangle.$$

Note, this is the $M_L=1$ component of the 1D state; it is, of course, not a 1P state because no such state exists for two equivalent p electrons.

4. What is the CI matrix element coupling $|1s^2 2s^2|$ and $|1s^2 3s^2|$?

These two determinants differ by two spin-orbitals, so

$$\langle |1s \uparrow 1s \downarrow 2s \uparrow 2s \downarrow | H | 1s \uparrow 1s \downarrow 3s \uparrow 3s \downarrow \rangle = \langle 2s 2s | 3s 3s \rangle = \langle 2s 3s | 3s 2s \rangle$$

(note, this is an exchange-type integral).

5. What is the CI matrix element coupling $|1s^2 2s^2|$ and $|1s^2 3s^2|$?

These two determinants differ by two spin-orbitals, so

$$\langle \psi | H | \psi \rangle = \langle \psi | \psi \rangle = \langle \psi | \psi \rangle$$

(note, again this is an exchange-type integral).

6. What is the Hamiltonian matrix element coupling $|\psi\rangle$ and $2^{-1/2} [|\psi_1 \uparrow \downarrow\rangle - |\psi_2 \uparrow \downarrow\rangle]$?

The first determinant differs from the 2 determinant by one spin-orbital, as does the second (after it is placed into maximal coincidence by making one permutation), so

$$\begin{aligned} & \langle \psi | H | 2^{-1/2} [|\psi_1 \uparrow \downarrow\rangle - |\psi_2 \uparrow \downarrow\rangle] \rangle \\ &= 2^{-1/2} [\langle \psi | \psi_1 \uparrow \downarrow \rangle + \langle \psi | \psi_2 \uparrow \downarrow \rangle] - (-1) 2^{-1/2} [\langle \psi | \psi_1 \uparrow \downarrow \rangle + \langle \psi | \psi_2 \uparrow \downarrow \rangle] \\ &= 2^{1/2} [\langle \psi | \psi_1 \uparrow \downarrow \rangle + \langle \psi | \psi_2 \uparrow \downarrow \rangle]. \end{aligned}$$

7. What is the element coupling $|\psi\rangle$ and $2^{-1/2} [|\psi_1 \uparrow \uparrow\rangle + |\psi_2 \uparrow \uparrow\rangle]$?

$$\begin{aligned} & \langle \psi | H | 2^{-1/2} [|\psi_1 \uparrow \uparrow\rangle + |\psi_2 \uparrow \uparrow\rangle] \rangle \\ &= 2^{-1/2} [\langle \psi | \psi_1 \uparrow \uparrow \rangle + \langle \psi | \psi_2 \uparrow \uparrow \rangle] + (-1) 2^{-1/2} [\langle \psi | \psi_1 \uparrow \uparrow \rangle + \langle \psi | \psi_2 \uparrow \uparrow \rangle] = 0. \end{aligned}$$

This result should not surprise you because $|\psi\rangle$ is an $S=0$ singlet state while $2^{-1/2} [|\psi_1 \uparrow \uparrow\rangle + |\psi_2 \uparrow \uparrow\rangle]$ is the $M_S=0$ component of the $S=1$ triplet state.

8. What is the $\mathbf{r} = \sum_j e_j \mathbf{r}_j$ electric dipole matrix element between $|\psi_1 \uparrow \downarrow\rangle$ and $2^{-1/2} [|\psi_1 \uparrow \downarrow\rangle + |\psi_2 \uparrow \downarrow\rangle]$? Is the second function a singlet or triplet? It is a singlet in disguise; by interchanging the p_0 and p_1 and thus introducing a (-1) , this function is clearly identified as $2^{-1/2} [|\psi_1 \uparrow \downarrow\rangle - |\psi_2 \uparrow \downarrow\rangle]$ which is a singlet.

The first determinant differs from the latter two by one spin orbital in each case, so

$$\begin{aligned} & \langle \psi_1 \uparrow \downarrow | \mathbf{r} | 2^{-1/2} [|\psi_1 \uparrow \downarrow\rangle + |\psi_2 \uparrow \downarrow\rangle] \rangle = \\ & 2^{-1/2} [\langle \psi_1 \uparrow \downarrow | \mathbf{r} | \psi_1 \uparrow \downarrow \rangle + \langle \psi_1 \uparrow \downarrow | \mathbf{r} | \psi_2 \uparrow \downarrow \rangle] = 2^{1/2} \langle \psi_1 \uparrow \downarrow | \mathbf{r} | \psi_2 \uparrow \downarrow \rangle. \end{aligned}$$

9. What is the electric dipole matrix elements between the $1^1 = |1 \ 1 \ 1 \ 1 \rangle$ state and the $1^1 = 2^{-1/2}[|1 \ 1 \ -1 \ 1 \rangle + |1 \ -1 \ 1 \ 1 \rangle]$ state?

$$\langle 2^{-1/2}[|1 \ 1 \ -1 \ 1 \rangle + |1 \ -1 \ 1 \ 1 \rangle] | \mathbf{r} | 1 \ 1 \ 1 \ 1 \rangle$$

$$= 2^{-1/2}[\langle -1 | \mathbf{r} | 1 \rangle + \langle -1 | \mathbf{r} | 1 \rangle]$$

$$= 2^{1/2} \langle -1 | \mathbf{r} | 1 \rangle.$$

10. As another example of the use of the SC rules, consider the configuration interaction which occurs between the $1s^2 2s^2$ and $1s^2 2p^2 \ ^1S$ CSFs in the Be atom.

The CSFs corresponding to these two configurations are as follows:

$$1 = |1s \ 1s \ 2s \ 2s \rangle$$

and

$$2 = 1/\sqrt{3} [|1s \ 1s \ 2p_0 \ 2p_0 \rangle - |1s \ 1s \ 2p_1 \ 2p_{-1} \rangle$$

$$- |1s \ 1s \ 2p_{-1} \ 2p_1 \rangle].$$

The determinantal Hamiltonian matrix elements needed to evaluate the 2×2 $H_{K,L}$ matrix appropriate to these two CSFs are evaluated via the SC rules. The first such matrix element is:

$$\langle |1s \ 1s \ 2s \ 2s \rangle | H | 1s \ 1s \ 2s \ 2s \rangle$$

$$= 2h_{1s} + 2h_{2s} + J_{1s,1s} + 4J_{1s,2s} + J_{2s,2s} - 2K_{1s,2s},$$

where

$$h_i = \langle i | -\hbar^2/2m_e \nabla^2 - 4e^2/r | i \rangle,$$

$$J_{i,j} = \langle i \ j | e^2/r_{12} | i \ j \rangle,$$

and

$$K_{ij} = \langle \psi_i | e^2/r_{12} | \psi_j \rangle$$

are the orbital-level one-electron, coulomb, and exchange integrals, respectively.

Coulomb integrals J_{ij} describe the coulombic interaction of one charge density (ψ_i^2 above) with another charge density (ψ_j^2 above); exchange integrals K_{ij} describe the interaction of an overlap charge density (i.e., a density of the form $\psi_i \psi_j$) with itself ($\psi_i \psi_j$ with $\psi_i \psi_j$ in the above).

The spin functions α and β which accompany each orbital in $|1s \uparrow 1s \downarrow 2s \uparrow 2s \downarrow\rangle$ have been eliminated by carrying out the spin integrations as discussed above. Because H contains no spin operators, this is straightforward and amounts to keeping integrals $\langle \psi_i | f | \psi_j \rangle$ only if ψ_i and ψ_j are of the same spin and integrals $\langle \psi_i \psi_j | g | \psi_k \psi_l \rangle$ only if ψ_i and ψ_k are of the same spin and ψ_j and ψ_l are of the same spin. The physical content of the above energy (i.e., Hamiltonian expectation value) of the $|1s \uparrow 1s \downarrow 2s \uparrow 2s \downarrow\rangle$ determinant is clear: $2h_{1s} + 2h_{2s}$ is the sum of the expectation values of the one-electron (i.e., kinetic energy and electron-nuclear coulomb interaction) part of the Hamiltonian for the four occupied spin-orbitals; $J_{1s,1s} + 4J_{1s,2s} + J_{2s,2s} - 2K_{1s,2s}$ contains the coulombic repulsions among all pairs of occupied spin-orbitals minus the exchange interactions among pairs of spin-orbitals with like spin.

The determinantal matrix elements linking ψ_1 and ψ_2 are as follows:

$$\langle |1s \uparrow 1s \downarrow 2s \uparrow 2s \downarrow | H | 1s \uparrow 1s \downarrow 2p_0 \uparrow 2p_0 \downarrow \rangle = \langle 2s \uparrow 2s \downarrow | 2p_0 \uparrow 2p_0 \downarrow \rangle,$$

$$\langle |1s \uparrow 1s \downarrow 2s \uparrow 2s \downarrow | H | 1s \uparrow 1s \downarrow 2p_1 \uparrow 2p_1 \downarrow \rangle = \langle 2s \uparrow 2s \downarrow | 2p_1 \uparrow 2p_1 \downarrow \rangle,$$

$$\langle |1s \uparrow 1s \downarrow 2s \uparrow 2s \downarrow | H | 1s \uparrow 1s \downarrow 2p_{-1} \uparrow 2p_{-1} \downarrow \rangle = \langle 2s \uparrow 2s \downarrow | 2p_{-1} \uparrow 2p_{-1} \downarrow \rangle,$$

where the Dirac convention has been introduced as a shorthand notation for the two-electron integrals (e.g., $\langle 2s \uparrow 2s \downarrow | 2p_0 \uparrow 2p_0 \downarrow \rangle$ represents $\int \int 2s^*(r_1) 2s^*(r_2) e^2/r_{12} 2p_0(r_1) 2p_0(r_2) dr_1 dr_2$).

The three integrals shown above can be seen to be equal and to be of the exchange-integral form by expressing the integrals in terms of integrals over cartesian functions and recognizing identities due to the equivalence of the $2p_x$, $2p_y$, and $2p_z$ orbitals. For example,

$$\langle 2s \uparrow 2s \downarrow | 2p_1 \uparrow 2p_1 \downarrow \rangle = (1 - 2)^2 \{ \langle 2s \uparrow 2s \downarrow | [2p_x + i 2p_y] [2p_x - i 2p_y] \rangle \} =$$

$$1/2 \{ \langle 2s \ 2s | x \ x \rangle + \langle 2s \ 2s | y \ y \rangle + i \langle 2s \ 2s | y \ x \rangle - i \langle 2s \ 2s | x \ y \rangle \} =$$

$$\langle 2s \ 2s | x \ x \rangle = K_{2s,x}$$

(here the two imaginary terms cancel and the two remaining real integrals are equal);

$$\langle 2s \ 2s \ 2p_0 \ 2p_0 \rangle = \langle 2s \ 2s | z \ z \rangle = \langle 2s \ 2s | x \ x \rangle = K_{2s,x}$$

(this is because $K_{2s,z} = K_{2s,x} = K_{2s,y}$);

$$\langle 2s \ 2s | 2p_{-1} 2p_1 \rangle = 1/2 \{ \langle 2s \ 2s | [2p_x - i 2p_y] [2p_x + i 2p_y] \rangle \} =$$

$$\langle 2s \ 2s | x \ x \rangle = \int \int 2s^*(r_1) 2s^*(r_2) e^2/r_{12} 2p_x(r_1) 2p_x(r_2) dr_1 dr_2 = K_{2s,x}.$$

These integrals are clearly of the exchange type because they involve the coulombic interaction of the $2s \ 2p_{x,y, \text{or } z}$ overlap charge density with itself.

Moving on, the matrix elements among the three determinants in \mathcal{H}_2 are given as follows:

$$\langle |1s \ 1s \ 2p_0 \ 2p_0 \rangle | H | 1s \ 1s \ 2p_0 \ 2p_0 \rangle$$

$$= 2h_{1s} + 2h_{2p} + J_{1s,1s} + J_{2p_z,2p_z} + 4J_{1s,2p} - 2K_{1s,2p}$$

($J_{1s,2p}$ and $K_{1s,2p}$ are independent of whether the $2p$ orbital is $2p_x$, $2p_y$, or $2p_z$);

$$\langle |1s \ 1s \ 2p_1 \ 2p_{-1} \rangle | H | 1s \ 1s \ 2p_1 \ 2p_{-1} \rangle$$

$$= 2h_{1s} + 2h_{2p} + J_{1s,1s} + 4J_{1s,2p} - 2K_{1s,2p} + \langle 2p_1 2p_{-1} | 2p_1 2p_{-1} \rangle;$$

$$\langle |1s \ 1s \ 2p_{-1} \ 2p_1 \rangle | H | 1s \ 1s \ 2p_{-1} \ 2p_1 \rangle$$

$$= 2h_{1s} + 2h_{2p} + J_{1s,1s} + 4J_{1s,2p} - 2K_{1s,2p} + \langle 2p_{-1} 2p_1 | 2p_{-1} 2p_1 \rangle;$$

$$\langle |1s \ 1s \ 2p_0 \ 2p_0 \rangle | H | 1s \ 1s \ 2p_1 \ 2p_{-1} \rangle = \langle 2p_0 2p_0 | 2p_1 2p_{-1} \rangle$$

$$\begin{aligned} \langle 1s \ 1s \ 2p_0 \ 2p_0 | H | 1s \ 1s \ 2p_{-1} \ 2p_1 \rangle &= \langle 2p_0 2p_0 | 2p_{-1} 2p_1 \rangle \\ \langle 1s \ 1s \ 2p_1 \ 2p_{-1} | H | 1s \ 1s \ 2p_{-1} \ 2p_1 \rangle &= \langle 2p_1 2p_{-1} | 2p_{-1} 2p_1 \rangle. \end{aligned}$$

Certain of these integrals can be recast in terms of cartesian integrals for which equivalences are easier to identify as follows:

$$\langle 2p_0 2p_0 | 2p_1 2p_{-1} \rangle = \langle 2p_0 2p_0 | 2p_{-1} 2p_1 \rangle = \langle z z | x x \rangle = K_{z,x};$$

$$\langle 2p_1 2p_{-1} | 2p_{-1} 2p_1 \rangle = \langle x x | y y \rangle + 1/2[\langle x x | x x \rangle - \langle x y | x y \rangle]$$

$$= K_{x,y} + 1/2 [J_{x,x} - J_{x,y}];$$

$$\langle 2p_1 2p_{-1} | 2p_1 2p_{-1} \rangle = \langle 2p_{-1} 2p_1 | 2p_{-1} 2p_1 \rangle = 1/2(J_{x,x} + J_{x,y}).$$

Finally, the 2x2 CI matrix corresponding to the CSFs ψ_1 and ψ_2 can be formed from the above determinantal matrix elements; this results in:

$$H_{11} = 2h_{1s} + 2h_{2s} + J_{1s,1s} + 4J_{1s,2s} + J_{2s,2s} - 2K_{1s,2s};$$

$$H_{12} = -K_{2s,x} / 3;$$

$$H_{22} = 2h_{1s} + 2h_{2p} + J_{1s,1s} + 4J_{1s,2p} - 2K_{1s,2p} + J_{z,z} - 2/3 K_{z,x}.$$

The lowest eigenvalue of this matrix provides this CI calculation's estimate of the ground-state 1S energy of Be; its eigenvector provides the CI amplitudes for ψ_1 and ψ_2 in this ground-state wavefunction. The other root of the 2x2 secular problem gives an approximation to another 1S state of higher energy, in particular, a state dominated by the $3^{-1/2} [|1s \ 1s \ 2p_0 \ 2p_0 \rangle - |1s \ 1s \ 2p_1 \ 2p_{-1} \rangle - |1s \ 1s \ 2p_{-1} \ 2p_1 \rangle]$ CSF.

11. As another example, consider the matrix elements which arise in electric dipole transitions between two singlet electronic states:

$\langle \psi_1 | \mathbf{E} \cdot \sum_i \mathbf{e}_i \mathbf{r}_i | \psi_2 \rangle$. Here $\mathbf{E} \cdot \sum_i \mathbf{e}_i \mathbf{r}_i$ is the one-electron operator describing the interaction of an electric field of magnitude and polarization \mathbf{E} with the instantaneous dipole moment

of the electrons (the contribution to the dipole operator arising from the nuclear charges $-Z_a e^2 \mathbf{R}_a$ does not contribute because, when placed between ψ_1 and ψ_2 , this zero-electron operator yields a vanishing integral because ψ_1 and ψ_2 are orthogonal).

When the states ψ_1 and ψ_2 are described as linear combinations of CSFs as introduced earlier ($\psi_i = \sum_K C_{iK} \Phi_K$), these matrix elements can be expressed in terms of CSF-based matrix elements $\langle \Phi_K | \sum_i \mathbf{e} \mathbf{r}_i | \Phi_L \rangle$. The fact that the electric dipole operator is a one-electron operator, in combination with the SC rules, guarantees that only states for which the dominant determinants differ by at most a single spin-orbital (i.e., those which are "singly excited") can be connected via electric dipole transitions through first order (i.e., in a one-photon transition to which the $\langle \psi_1 | \sum_i \mathbf{e} \mathbf{r}_i | \psi_2 \rangle$ matrix elements pertain). It is for this reason that light with energy adequate to ionize or excite deep core electrons in atoms or molecules usually causes such ionization or excitation rather than double ionization or excitation of valence-level electrons; the latter are two-electron events.

In, for example, the $\pi \rightarrow \pi^*$ excitation of an olefin, the ground and excited states are dominated by CSFs of the form (where all but the "active" π and π^* orbitals are not explicitly written):

$$\psi_1 = | \dots \pi \dots |$$

and

$$\psi_2 = 1/\sqrt{2} [| \dots \pi^* \dots | - | \dots \pi \dots |].$$

The electric dipole matrix element between these two CSFs can be found, using the SC rules, to be

$$e/\sqrt{2} [\langle \dots \pi^* \dots | \mathbf{r} | \dots \pi \dots \rangle + \langle \dots \pi \dots | \mathbf{r} | \dots \pi^* \dots \rangle] = \sqrt{2} e \langle \dots \pi^* \dots | \mathbf{r} | \dots \pi \dots \rangle.$$

Notice that in evaluating the second determinantal integral $\langle \dots \pi \dots | \mathbf{e} \mathbf{r} | \dots \pi^* \dots \rangle$, a sign change occurs when one puts the two determinants into maximum coincidence; this sign change then makes the minus sign in ψ_2 yield a positive sign in the final result.

IV. Summary

In all of the above examples, the SC rules were used to reduce matrix elements of one- or two- electron operators between determinantal functions to one- or two- electron integrals over the orbitals which appear in the determinants. In any ab initio electronic structure computer program there must exist the capability to form symmetry-adapted CSFs and to evaluate, using these SC rules, the Hamiltonian and other operators' matrix elements among these CSFs in terms of integrals over the mos that appear in the CSFs. The SC rules provide not only the tools to compute quantitative matrix elements; they allow one to understand in qualitative terms the strengths of interactions among CSFs. In the following section, the SC rules are used to explain why chemical reactions in which the reactants and products have dominant CSFs that differ by two spin-orbital occupancies often display activation energies that exceed the reaction endoergicity.