1.20: Calculating Orbital Energies and Expansion Coefficients

Calculation of the orbital energies and expansion coefficients is based on the *variation principle*, which states that any approximate wavefunction must have a higher energy than the true wavefunction. This follows directly from the fairly common-sense idea that in general any system tries to minimize its energy. If an 'approximate' wavefunction had a lower energy than the 'true' wavefunction, we would expect the system to try and adopt this 'approximate' lower energy state, rather than the 'true' state. That all approximations to the true wavefunction must have a higher energy than the true wavefunction is the only scenario that makes physical sense. A mathematical proof of the variation principle is given in the Appendix.

We apply the variation principle as follows:

Molecular energy levels, or orbital energies, are eigenvalues of the molecular Hamiltonian $\hat{H}$. Using a standard result from quantum mechanics, it follows that the energy E of a molecular orbital Ψ is

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad \text{(unnormalized } \Psi\text{)}$$

$$\text{or} \quad E = \langle \Psi | \hat{H} | \Psi \rangle \quad \text{(normalized } \Psi \text{, for which} \langle \Psi | \Psi \rangle = 1)$$

(1.20.1)

If the true wavefunction has the lowest energy, then to find the closest approximation we can to the true wavefunction, all we have to do is find the coefficients in our expansion of SALCs that minimize the energy in the above expressions. In practice, we substitute our wavefunction and minimize the resulting expression with respect to the coefficients. To show how this is done, we'll use our NH_3 wavefunction of A_1 symmetry from the previous section. Substituting into Equation 1.20.1 gives:

$$
\begin{aligned}
E &= \frac{\langle c_1\phi_1 + c_2\phi_2 | \hat{H} | c_1\phi_1 + c_2\phi_2 \rangle}{\langle c_1\phi_1 + c_2\phi_2 | c_1\phi_1 + c_2\phi_2 \rangle} \\
&= \frac{\langle c_1\phi_1 | \hat{H} | c_1\phi_1 \rangle + \langle c_1\phi_1 | \hat{H} | c_2\phi_2 \rangle + \langle c_2\phi_2 | \hat{H} | c_1\phi_1 \rangle + \langle c_2\phi_2 | \hat{H} | c_2\phi_2 \rangle}{\langle c_1\phi_1 | c_1\phi_1 \rangle + \langle c_1\phi_1 | c_2\phi_2 \rangle + \langle c_2\phi_2 | c_1\phi_1 \rangle + \langle c_2\phi_2 | c_2\phi_2 \rangle} \\
&= \frac{c_1^2 \langle \phi_1 | \hat{H} | \phi_1 \rangle + c_1 c_2 \langle \phi_1 | \hat{H} | \phi_2 \rangle + c_2 c_1 \langle \phi_2 | \hat{H} | \phi_1 \rangle + c_2^2 \langle \phi_2 | \hat{H} | \phi_2 \rangle}{c_1^2 \langle \phi_1 | \phi_1 \rangle + c_1 c_2 \langle \phi_1 | \phi_2 \rangle + c_2 c_1 \langle \phi_2 | \phi_1 \rangle + c_2^2, \phi_2 | \phi_2 \rangle}
\end{aligned}
$$

(1.20.2)

If we now define a Hamiltonian matrix element $H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle$ and an overlap integral $S_{ij} = \langle \phi_i | \phi_j \rangle$ and note that $H_{ij} = H_{ji}$ and $S_{ij} = S_{ji}$, this simplifies to

$$E = \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}}$$

(1.20.3)

To get this into a simpler form for carrying out the energy minimization, we multiply both sides through by the denominator to give

$$E(c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}) = c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}$$

(1.20.4)

Now we need to minimize the energy with respect to c_1 and c_2, i.e., we require

$$\frac{\partial E}{\partial c_1} = 0$$

(1.20.5)

and

$$\frac{\partial E}{\partial c_2} = 0$$

(1.20.6)

If we differentiate the above equation through separately by c_1 and c_2 and apply this condition, we will end up with two equations in the two unknowns c_1 and c_2, which we can solve to determine the coefficients and the energy.

Differentiating Equation 1.20.4 with respect to c_1 (via the product rule of differentiation) gives

$$\frac{\partial E}{\partial c_1}(c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}) + E(2c_1 S_{11} + 2c_2 S_{12}) = 2c_1 H_{11} + 2c_2 H_{12}$$

(1.20.7)

Differentiating Equation 1.20.4 with respect to c_2 gives

$$\frac{\partial E}{\partial c_2}(c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}) + E(2c_1 S_{12} + 2c_2 S_{22}) = 2c_1 H_{12} + 2c_2 H_{22} \tag{1.20.8}$$

Because

$$\frac{\partial E}{\partial c_1} = \frac{\partial E}{\partial c_2} = 0 \tag{1.20.9}$$

the first term on the left hand side of both equations is zero, leaving us with

$$
\begin{aligned}
E(2c_1 S_{11} + 2c_2 S_{12}) &= 2c_1 H_{11} + 2c_2 H_{12} \\
E(2c_1 S_{12} + 2c_2 S_{22}) &= 2c_1 H_{12} + 2c_2 H_{22}
\end{aligned}
\tag{1.20.10}
$$

These are normally rewritten slightly, in the form

$$
\begin{aligned}
c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) &= 0 \\
c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) &= 0
\end{aligned}
\tag{1.20.11}
$$

Equations 1.20.11 are known as the **secular equations** and are the set of equations we need to solve to determine c_1, c_2, and E. In the general case (derived in the Appendix), when our wavefunction is a linear combination of N SALCs (i.e. $\Psi = \Sigma_{i=1}^{N} c_i \phi_i$) we get N equations in N unknowns, with the kth equation given by

$$\sum_{i=1}^{N} c_i(H_{ki} - ES_{ki}) = 0 \tag{1.20.12}$$

Note that we can use any basis functions we like together with the linear variation method described here to construct approximate molecular orbitals and determine their energies, but choosing to use SALCs simplifies things considerably when the number of basis functions is large. An arbitrary set of N basis functions leads to a set of N equations in N unknowns, which must be solved simultaneously. Converting the basis into a set of SALCs separates the equations into several smaller sets of secular equations, one for each irreducible representation, which can be solved independently. It is usually easier to solve several sets of secular equations of lower dimensionality than one set of higher dimensionality.