Appendix B

B.1 The Variational Principle

The *Variational Principle* states that an approximate wave function has an energy that is above or equal to the exact energy. The equality holds only if the wave function is exact. The proof is as follows.

Assume that we know the exact solutions to the Schrödinger equation.

$$\mathbf{H}\Psi_i = E_i\psi_i \quad i = 0, 1, 2, \ldots \infty \tag{B.1}$$

There are infinitely many solutions and we assume that they are labelled according to their energies, E_0 being the lowest. Since the **H** operator is Hermitian, the solutions form a *complete* basis. We may furthermore choose the solutions to be orthogonal and normalized.

$$\langle \Psi_i | \Psi_j \rangle = \delta_{ij} \tag{B.2}$$

An approximate wave function can be expanded in the exact solutions, since they form a complete set.

$$\Phi = \sum_{i=0}^{\infty} a_i \Psi_i \tag{B.3}$$

The energy of an approximate wave function is calculated as in eq. (B.4).

$$W = \frac{\langle \Phi | \mathbf{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} \tag{B.4}$$

Inserting the expansion (B.3) we obtain eq. (B.5).

$$W = \frac{\sum_{i=0}^{\infty} \sum_{j=0}^{\infty} a_i a_j \langle \Psi_i | \mathbf{H} | \Psi_j \rangle}{\sum_{i=0}^{\infty} \sum_{j=0}^{\infty} a_i a_j \langle \Psi_i | \Psi_j \rangle} \tag{B.5}$$

Using the fact that $\mathbf{H}\Psi_i = E_i\Psi_i$ and the orthonormality of the Ψ_i (eqs (B.1) and (B.2)), we obtain eq. (B.6).

$$W = \frac{\sum_{i=0}^{\infty} a_i^2 E_i}{\sum_{i=0}^{\infty} a_i^2} \tag{B.6}$$

The variational principle states that $W \geq E_0$ or, equivalently, $W - E_0 \geq 0$.

$$W - E_0 = \frac{\sum_{i=0}^{\infty} a_i^2 E_i}{\sum_{i=0}^{\infty} a_i^2} - E_0 = \frac{\sum_{i=0}^{\infty} a_i^2 (E_i - E_0)}{\sum_{i=0}^{\infty} a_i^2} \geq 0 \tag{B.7}$$

Since a_i^2 is always positive or zero, and $E_i - E_0$ is always positive or zero (E_0 is by definition the lowest energy), this completes the proof. Furthermore, in order for the equal sign to hold, all $a_{i\neq 0} = 0$ since $E_{i\neq 0} - E_0$ is non-zero (neglecting degenerate ground states). This in turns means that $a_0 = 1$, owing to the normalization of Φ, and consequently the wave function is the exact solution.

This proof shows that any approximate wave function will have an energy above or equal to the exact ground state energy. There is a related theorem, known as *MacDonald's Theorem*, which states that the nth root of a set of secular equations (e.g. a CI matrix) is an upper limit to the $(n-1)$th excited exact state, within the given symmetry subclass.[1] In other words, the lowest root obtained by diagonalizing a CI matrix is an upper limit to the lowest exact wave functions, the second root is an upper limit to the exact energy of the first excited state, the third root is an upper limit to the exact second excited state, and so on.