THE VARIATIONAL PRINCIPLE

The variational principle asserts that if $\tilde{\psi}$ is an arbitrary wavefunction satisfying the boundary conditions for a system, then the expectation value of its energy, $\tilde{E}$, provides an upper bound to the lowest eigenvalue of the Hamiltonian, E_0. That is,

$$\tilde{E} \equiv \frac{\left\langle \tilde{\psi} \middle| \hat{H} \middle| \tilde{\psi} \right\rangle}{\left\langle \tilde{\psi} \middle| \tilde{\psi} \right\rangle} \geq E_0. \tag{1}$$

Note that Dirac notation has been used.

We can prove this as follows. Suppose the Hamiltonian $\hat{H}$ has a set of associated wavefunctions ψ_k that form a complete set[1], i.e.,

$$\hat{H}\psi_k = E_k \psi_k \tag{2}$$

Now, any arbitrary wavefunction of the Hamiltonian operator *satisfying the boundary conditions* of a system can be expanded using a linear combination of the complete eigenfunctions. We can therefore write $\tilde{\psi}$ in terms of the normalised eigenfunctions of the Hamiltonian $\hat{H}$:

$$\tilde{\psi} = \sum_k c_k \psi_k \tag{3}$$

The numerator in Eq. 1 then becomes

$$\begin{aligned}
\left\langle \tilde{\psi} \middle| \hat{H} \middle| \tilde{\psi} \right\rangle &= \left\langle \sum_k c_k \psi_k \middle| \hat{H} \middle| \sum_l c_l \psi_l \right\rangle \\
&= \sum_k \sum_l c_k^* c_l \left\langle \psi_k \right| \hat{H} \left| \psi_l \right\rangle \\
&= \sum_{kl} c_k^* c_l \left\langle \psi_k \right| E_l \left| \psi_l \right\rangle \\
&= \sum_{kl} c_k^* c_l E_l \left\langle \psi_k | \psi_l \right\rangle \\
&= \sum_{kl} c_k^* c_l E_l \delta_{kl} \\
&= \sum_l c_l^* c_l E_l \\
&= \sum_l |c_l|^2 E_l
\end{aligned} \tag{4}$$

[1]We will prove the completeness of the eigenfunctions elsewhere.

where we have used the eigenvalue equation (Eq. 2) in going from second to third line, and the orthonomality of the eigenfunctions $\langle \psi_k | \psi_l \rangle = \delta_{kl}$ in going from fourth to fifth line; in going from fifth to sixth line, we note that summation over the Kronecker delta "picks out" the values for which the indices are the same since

$$\delta_{kl} = \begin{cases} 1, & \text{if } k = l \\ 0, & \text{if } k \neq l \end{cases} \tag{5}$$

Similarly, the denominator is given by

$$\begin{aligned} \left\langle \tilde{\psi} \middle| \tilde{\psi} \right\rangle &= \left\langle \sum_k c_k \psi_k \middle| \sum_l c_l \psi_l \right\rangle \\ &= \sum_k \sum_l c_k^* c_l \langle \psi_k | \psi_l \rangle \\ &= \sum_{kl} c_k^* c_l \langle \psi_k | \psi_l \rangle \\ &= \sum_{kl} c_k^* c_l \delta_{kl} \\ &= \sum_l c_l^* c_l \\ &= \sum_l |c_l|^2 \end{aligned} \tag{6}$$

Now, substituting the equations for the numerator and denominator (Eqs. 4 and 6) into Eq. 1, we have

$$\tilde{E} \equiv \frac{\left\langle \tilde{\psi} \middle| \hat{H} \middle| \tilde{\psi} \right\rangle}{\left\langle \tilde{\psi} \middle| \tilde{\psi} \right\rangle} = \frac{\sum_l |c_l|^2 E_l}{\sum_l |c_l|^2} \tag{7}$$

The variational result follows directly as the following:

$$\tilde{E} - E_0 = \frac{\sum_l |c_l|^2 E_l}{\sum_l |c_l|^2} - \frac{\sum_l |c_l|^2 E_0}{\sum_l |c_l|^2} = \frac{\sum_l |c_l|^2 (E_l - E_0)}{\sum_l |c_l|^2} \geq 0 \tag{8}$$

where the first equality follows as E_0 is a constant that is not affected by the summation over the index l and the last follows since $E_l \geq E_0$ for all l as E_0 is the ground state energy.

We can see that the energy from the trial wavefunction will be the same as the ground state energy, $\tilde{E} = E_0$, only if all the c_l coefficients are zero for states with $E_l > E_0$. We can see that to get the energy exactly right, we have to get the wavefunction exactly right. It is also true that the better the approximation the trial wavefunction is to the true wavefunction, the better the approximation to the true ground state energy.