

THE VARIATION PRINCIPLE

In everything that follows we assume that the Born-Oppenheimer approximation is valid.

Because we can never deal with a **complete** set of basis functions, any ‘many-electron’ wavefunctions that we calculate are only approximate solutions to the Schrödinger equation.

One of the most important tools we have to deal with approximate wavefunctions is the **variation principle**. This asserts that if $\tilde{\psi}$ is an arbitrary wavefunction satisfying the boundary conditions for the problem, then the expectation value of its energy, $\tilde{E} = \langle \mathcal{H} \rangle$, is always greater than or equal to the true ground state energy E_0 .

That is, if $\tilde{\psi}$ is normalised,

$$\tilde{E} \equiv \langle \tilde{\psi} | \mathcal{H} | \tilde{\psi} \rangle \geq E_0 \quad (1)$$

If the equality holds, the $\tilde{\psi}$ must be the true ground state eigenfunction.

Hence, if $\tilde{\psi}$ contains any variable parameters, it follows that the best wavefunction is obtained by minimizing \tilde{E} .

Proof:

Let’s say we can expand the approximate (or trial) wavefunction, $\tilde{\psi}$, in terms of the **complete** set of orthonormal eigenfunctions of the **exact** Hamiltonian, $\{\phi_i\}$. Because these exact eigenfunctions themselves form a complete set we can always expand any approximate wavefunction in terms of them (even if we don’t know what they are!).

The approximate wavefunction $\tilde{\psi}$ is written as:

$$\tilde{\psi} = \sum_k c_k \phi_k$$

Then, since we assume that $\tilde{\psi}$ is normalised:

$$\begin{aligned} 1 = \langle \tilde{\psi} | \tilde{\psi} \rangle &= \sum_{kl} c_k^* c_l \langle \phi_k | \phi_l \rangle \\ &= \sum_{kl} c_k^* c_l \delta_{kl} \\ &= \sum_k |c_k|^2 \end{aligned}$$

and

$$\begin{aligned} \tilde{E} &= \langle \tilde{\psi} | \mathcal{H} | \tilde{\psi} \rangle \\ &= \sum_{kl} c_k^* c_l \langle \phi_k | \mathcal{H} | \phi_l \rangle \\ &= \sum_{kl} c_k^* c_l \langle \phi_k | E_l | \phi_l \rangle \\ &= \sum_{kl} c_k^* c_l E_l \delta_{kl} \\ &= \sum_k |c_k|^2 E_k \end{aligned}$$

So, if E_0 is the ground state energy,

$$\begin{aligned}\tilde{E} - E_0 &= \sum_k |c_k|^2 (E_k - E_0) \\ &\geq 0 \quad \text{since} \quad \sum_k |c_k|^2 = 1 \quad \text{and} \quad E_k \geq E_0\end{aligned}$$

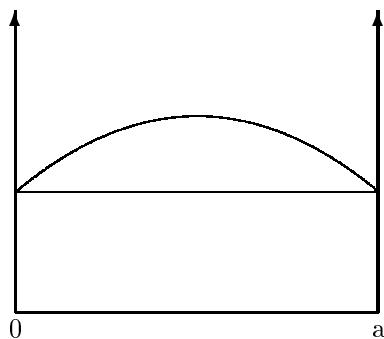
Note that $\tilde{E} = E_0$ only if all the c_k are zero for states with $E_k > E_0$. That is, to get the energy exactly right we have to get the wavefunction exactly right.

However, a good approximation to the wavefunction will yield a good approximation to the energy.

Example: Variation principle for a particle in a box.

Suppose that we did not know the ground-state wavefunction for the particle in a box. Knowing that it has to be zero when $x = 0$ and $x = a$, we might try the wavefunction:

$$\tilde{\psi} = x(a - x)$$



For this wavefunction we find:

$$\begin{aligned}\langle \tilde{\psi} | \tilde{\psi} \rangle &= \int_0^a x^2 (a - x)^2 dx = \frac{a^5}{30} \\ \langle \tilde{\psi} | \mathcal{H} | \tilde{\psi} \rangle &= -\frac{\hbar^2}{2m} \int_0^a x(a - x) \frac{d^2}{dx^2} x(a - x) dx \\ &= \frac{\hbar^2}{2m} \frac{a^3}{3}, \quad \text{so,} \\ \tilde{E} &= \langle \mathcal{H} \rangle = \frac{10\hbar^2}{2ma^2}\end{aligned}$$

The exact energy for the ground state of the particle in a box is $\frac{\hbar^2}{8ma^2}$, so the approximate result is higher than the exact one by a factor of $\frac{10}{\pi^2} = 1.013$. The wavefunction is not correct, but it gives a good estimate of the energy.

Exercise

The 'quartic oscillator' has the Hamiltonian

$$\mathcal{H} = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2} x^4$$

Find the expectation value of the energy for the trial wavefunction $\exp[-\frac{1}{2}\alpha q^2]$, and show that the energy is minimized when $\alpha = 3^{\frac{1}{3}}$.