VARIATIONS

These are the most widely used methods in quantum chemistry. An exact wavefunction satisfies

$$H\psi_n = E_n\psi_n, \Rightarrow \quad E_n = \frac{\langle\psi_n|H|\psi_n\rangle}{\langle\psi_n|\psi_n\rangle}.$$

The energy functional (=function of a function) is therefore defined by

$$E'[\phi] \equiv \frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle}.$$

E' is an upper bound to the ground state energy.

proof

ϕ may be spanned by the set of all eigenfunctions ψ_n of H, $\phi = \sum_n a_n\psi_n$. Substituting in the equation for E',

$$E' = \frac{\sum_{nm} a_n^* a_m \langle\psi_n|H|\psi_m\rangle}{\sum_{nm} a_n^* a_m \langle\psi_n|\psi_m\rangle} = \frac{\sum_{nm} a_n^* a_m E_m \langle\psi_n|\psi_m\rangle}{\sum_{nm} a_n^* a_m \langle\psi_n|\psi_m\rangle} =$$

$$= \frac{\sum_n |a_n|^2 E_n}{\sum_n |a_n|^2} \geq \frac{\sum_n |a_n|^2 E_1}{\sum_n |a_n|^2} = E_1.$$

The inequality occurs because E_1 is the ground state energy, therefore $E_n \geq E_1$.

To have equality ($=$ rather than $\geq$), a_n must vanish unless $E_n = E_1$, meaning that only ψ_n with energy E_1 appear in the expansion of ϕ. In this case, ϕ is also an eigenfunction of H with the eigenvalue E_1.

The lower E' is, the closer it is to the real ground state energy. It can be shown that the error in the energy is of second order, so that rather good energies are obtained.

Define $\phi = \psi_1 + \alpha\chi$, where the functions ψ_1 (the ground state wavefunction) and χ are normalized, and the parameter α gives the size of the error.

$$E'[\phi] - E_1 = \frac{\langle\phi|H - E_1|\phi\rangle}{\langle\phi|\phi\rangle} = \frac{\langle\psi_1 + \alpha\chi|H - E_1|\psi_1 + \alpha\chi\rangle}{\langle\phi|\phi\rangle}.$$

Since $(H - E_1)|\psi_1\rangle = 0$ and $\langle\psi_1|(H - E_1) = 0$ (Hermitian conjugate),

$$E'[\phi] - E_1 = \frac{\langle\alpha\chi|H - E_1|\alpha\chi\rangle}{\langle\phi|\phi\rangle} = |\alpha|^2\,\frac{\langle\chi|H - E_1|\chi\rangle}{\langle\phi|\phi\rangle}.$$

The error in the energy is of order $|\alpha|^2$, and if α is small $|\alpha|^2$ is even smaller. Note this applies to the energy only and not to other observables.

Applications of variational methods involve the choice of some trial function $\phi(\underline{q};\underline{\alpha})$, with free parameters $\underline{\alpha}$. The energy is

$$E'[\phi] = \frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle} = E'(\underline{\alpha})$$

and the values of $\underline{\alpha}$ giving minimal E' are found.

The minimization of E is a technical mathematical problem, which may in certain cases be very difficult. The major step in applying variational methods is the selection of the form of ϕ, which involves physical considerations, understanding the character of the system and interactions in it.

Examples:

Particle in an infinite box:

$$V = \begin{cases} 0 & 0 \le x \le l \\ \infty & \text{elsewhere} \end{cases} \qquad \phi = \begin{cases} x(l-x) & 0 \le x \le l \\ 0 & \text{elsewhere} \end{cases}$$

$$E' = \frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle} = \frac{5h^2}{4\pi^2 l^2 m} > E_1 = \frac{h^2}{8ml^2}$$

The error here is 1.3%. Note there was no free parameter.

Harmonic oscillator, $H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$.

A trial function: $\phi(x) = \begin{cases} (\alpha^2 - x^2) & |x| < \alpha \\ 0 & |x| > \alpha \end{cases}$.

The energy is found to be $E'(\alpha) = \frac{5}{4}\frac{\hbar^2}{m\alpha^2} + \frac{1}{14}m\omega^2\alpha^2$.

Minimization: $\frac{dE'}{d\alpha} = 0 \quad \Rightarrow \quad \alpha^2 = \sqrt{\frac{35}{2}}\frac{\hbar}{m\omega} \quad \Rightarrow \quad E' = 0.598\hbar\omega$.
This is higher than the lowest eigenvalue, which is $0.5\hbar\omega$.

Another trial function: $\phi(x) = e^{-\gamma x^2}$.

$$E'(\gamma) = \frac{m\omega^2}{8\gamma} + \frac{\hbar^2}{2m}\gamma$$

$$\frac{dE'}{d\gamma} = -\frac{m\omega^2}{8\gamma^2} + \frac{\hbar^2}{2m} = 0$$

$$\gamma^2 = m^2\frac{\omega^2}{4\hbar^2} \quad \gamma = \frac{1}{2}\frac{m\omega}{\hbar} \quad E' = \frac{1}{2}\hbar\omega.$$

Here we got the exact ground state energy, because the form of ϕ included the exact wavefunction.

For real, complicated systems, variational functions must have a large number of variation parameters. In practice, the optimization of so many parameters is an insurmountable problem in the general case. The only form of variational functions allowing simultaneous optimization of very many parameters (in the millions) is a linear combination of a preselected set of functions, when the combination coefficients are the variational parameters. The vast majority of variational calculations for atoms and molecules use therefore linear variations.

A finite set of functions is selected to span approximately the