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Approximate Methods in Quantum Mechanics:

Exact solutions of Schrodinger equation for an arbitrary system are not always easy to find. As usual, one resorts to approximations to gain some information about the energy eigenvalues and eigenstates in such cases.

There are well known approximate methods to deal with this. The precision of approximations depend on how accurate a result we need (compared with what can be experimentally measured). The result can be improved numerically by following the recipe and using computers.

Here we discuss two important approximations: the Rayleigh-Ritz variational method, and the WKB approximation.

Rayleigh-Ritz Variational Method:

Recall that for an arbitrary state vector $|\psi\rangle$, we have:

$$\langle\psi|H|\psi\rangle = \sum_n \langle\psi_n|\psi_n\rangle |a_n|^2 E_n = \sum_n |a_n|^2 E_n$$

Here $|\psi\rangle = \sum_n a_n |\psi_n\rangle$, where $|\psi_n\rangle$ are energy eigenstates with corresponding eigenvalues E_n. Since $|a_n|^2 \leq 1$ (for normalized state vectors), we then have:

$$\langle\psi|H|\psi\rangle \geq E_0 \qquad (E_0: \text{the ground state energy})$$

Thus $\langle\psi|H|\psi\rangle$ provides an upper bound on E_0. One can choose $|\psi\rangle$ to make $\langle H\rangle$ sufficiently close to E_0. For example, consider the potential $V = \lambda x^4$. As the trial function, lets choose the Gaussian wavepacket $\psi(x) = \left(\frac{\pi}{\alpha}\right)^{\frac{1}{4}} e^{-\frac{1}{2}\alpha x^2}$. Now:

$$\langle H\rangle_{(\alpha)} = \int \left(\frac{\pi}{\alpha}\right)^{-\frac{1}{2}} e^{-\frac{\alpha x^2}{2}} \left[-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \lambda x^4\right] e^{-\frac{\alpha x^2}{2}}\, dx$$

$$= \frac{\hbar^2\alpha}{4m} + 3\frac{\lambda}{4\alpha^2}$$

Note that $\langle H \rangle_{(\alpha)}$ is a function of α. For all α we know that $\langle H \rangle_{(\alpha)} \geq E_0$. We therefore get a better estimate if we make $\langle H \rangle_{(\alpha)}$ as small as possible. The minimum of $\langle H \rangle_{(\alpha)}$ is obtained at:

$$\alpha_0 = \left(\frac{6m\lambda}{\hbar^2}\right)^{\frac{1}{3}} \Rightarrow \langle H \rangle_{(\alpha_0)} = \frac{3}{8}\left(\frac{6\hbar^4\lambda}{m^2}\right)^{\frac{1}{2}}$$

Since $V_{(x)}$ is positive definite, we know that $E_0 > 0$.

Thus we have found:

$$0 \leq E_0 \leq \frac{3}{8}\left(\frac{6\hbar^4\lambda}{m^2}\right)^{\frac{1}{2}}$$

In general, we can use the properties of eigenstates of a system (obviously system dependent) to get a good estimate.

For the λx^4 potential, we know that because of the reflection symmetry of the potential, the energy eigenstates are even and odd functions (alternating

between the two). The ground state (as always) is an even function. Moreover, the ground state has no nodes (does not change sign). Therefore a good wavefunction that captures these two properties is an even one without any nodes.

We can also use Rayleigh-Ritz method to estimate the energy of excited levels. Lets assume we have a trial function with a main component from $|\Psi_1\rangle$ (the first excited level) and subdominant mixtures from the other states:

$$|\Psi\rangle \approx |\Psi_1\rangle + a_0|\Psi_1\rangle + a_2|\Psi_2\rangle + \dots \quad |a_0|, |a_2|, \dots \ll 1$$

Then:

$$\langle\Psi|H|\Psi\rangle \simeq E_1 + |a_0|^2 E_0 + |a_2|^2 E_2 + \dots$$

Note that $\frac{\partial E(\Psi_1)}{\partial a_0} = \frac{\partial E(\Psi_1)}{\partial a_2} = \dots = 0$, where

$E_{(\Psi)} \equiv \langle \Psi | H | \Psi \rangle$.

This implies that $E_{(\Psi)}$ has extrema at the energy eigenstates $|\Psi_1\rangle, |\Psi_2\rangle, \ldots$. Here we treat $E(\Psi)$ as a function defined over $\hat{}$ state vectors of a system (points in the Hilbert space). In principle if one could $E_{(\Psi)}$ for all $\Psi_{(x)}$, then $E_0, E_1, \ldots$ would be found by looking at the extrema of it.