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The <u>variational</u> <u>method</u> is useful when the system we wish to solve is not close to an exactly solvable system. It is mainly useful for finding the <u>ground state</u> energy and wavefunction. It is based on the following theorem:

Let $H|0\rangle = E_0|0\rangle$, where $|0\rangle$ is the ground state, assumed to be discrete and (for simplicity) nondegenerate. Let $|\psi\rangle$ be any state, not necessarily normalized. Then

$$\frac{\langle\psi|H_0|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0 .$$

First we prove this, then say what it is good for. Let $|\phi\rangle$ be the normalized version of $|\psi\rangle$,

$$|\phi\rangle = \frac{|\psi\rangle}{\sqrt{\langle\psi|\psi\rangle}} .$$

Then $\quad \langle\phi|\phi\rangle = 1 \quad$ and $\quad \dfrac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \langle\phi|H|\phi\rangle.$

Now decompose $|\phi\rangle$ into a part lying in the ground eigenspace and a part orthogonal to it,

$$|\phi\rangle = a|0\rangle + |\epsilon\rangle, \quad \text{where} \quad \langle 0|\epsilon\rangle = 0.$$

Then

$$1 = \langle\phi|\phi\rangle = |a|^2 + \langle\epsilon|\epsilon\rangle,$$

and

$$\begin{aligned}\langle\phi|H|\phi\rangle &= |a|^2\langle 0|H|0\rangle + a^*\langle 0|H|\epsilon\rangle + a\langle\epsilon|H|0\rangle + \langle\epsilon|H|\epsilon\rangle \\ &= |a|^2 E_0 \quad + \quad 0 \quad + 0 \quad + \quad \langle\epsilon|H|\epsilon\rangle\end{aligned}$$

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So,

$$\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \langle\phi|H|\phi\rangle = |a|^2 E_0 + \langle\varepsilon|H|\varepsilon\rangle$$

$$= E_0 + \langle\varepsilon|H|\varepsilon\rangle - E_0\langle\varepsilon|\varepsilon\rangle$$

$$= E_0 + \langle\varepsilon|(H-E_0)|\varepsilon\rangle \geq E_0$$

Since $H - E_0$ is a nonnegative operator, the 2nd term is $\geq E_0$.

Thus, if $|\psi\rangle$ is a (hopefully good) guess to the ground state $|0\rangle$, then by computing $\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}$ you get an upper bound to the gnd state energy E_0, which is hopefully close to E_0. $|\psi\rangle$ is called a <u>trial wavefn</u>.. If you have a family of trial wave fns, then the one that minimizes $\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}$ is the best estimate of $|0\rangle$, since it gives the energy closest to the true E_0. This is the variational criterion for the "best estimate"

In practice we usually choose a family of trial wave fns $|\psi(\lambda)\rangle$ where λ is one or more parameters. Then we define

$$F(\lambda) = \frac{\langle\psi(\lambda)|H|\psi(\lambda)\rangle}{\langle\psi(\lambda)|\psi(\lambda)\rangle}.$$

The minimum of F is at λ_0; it satisfies

$$\frac{\partial F}{\partial\lambda}(\lambda_0) = 0.$$

Then $F(\lambda_0)$ is an estimate (an upper bound) for E_0, and $|\psi(\lambda_0)\rangle$

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is an estimate for $|0\rangle$.

In practice, the denominators $\langle\psi(\lambda)|\psi(\lambda)\rangle$ can be awkward. One approach is just to require that all trial wave fns be normalized. Often what is easier is to enforce normalization by using Lagrange multipliers. This means that out of some family $|\psi(\lambda)\rangle$ of trial wave functions, of which only a subset is normalized, we minimize $\langle H\rangle$ w.r.t. only the normalized subset. To use the Lagrange multiplier method, we introduce the function

$$F(\lambda,\beta) = \langle\psi(\lambda)|H|\psi(\lambda)\rangle - \beta\left(\langle\psi(\lambda)|\psi(\lambda)\rangle - 1\right)$$

and then require

$$\frac{\partial F}{\partial\lambda} = 0 \quad \text{and} \quad \frac{\partial F}{\partial\beta} = 0.$$

The L.M. β is effectively another parameter. The 2nd eqn. implies normalization.

As an example of the L.M. method, let $\{|n\rangle\}$ be any basis (not usually the energy eigenbasis, since we don't know what that is). Then the unknown state $|\psi\rangle$ can be expanded in terms of the basis,

$$|\psi\rangle = \sum_{n=1}^{\infty} c_n |n\rangle.$$

There is no approximation in this.

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But in practice (on computers, etc) we can only handle a finite basis, so we write

$$|\psi\rangle = \sum_{n=1}^{N} c_n |n\rangle,$$

where N = finite, and take this as a trial wave fn. with parameters $\lambda = \{c_n\}$. Then

$$F(\lambda,\beta) = \sum_{n,m=1}^{N} c_n^* \langle n|H|m\rangle c_m - \beta \left(\sum_{n=1}^{N} |c_n|^2 - 1 \right).$$

The c_n are complex, so we want to vary w.r.t. their real and imag. parts. An equivalent procedure is to vary w.r.t. c_n and c_n^*, treated as independent complex #'s. This gives

$$\frac{\partial F}{\partial c_n^*} = \sum_{m=1}^{N} \langle n|H|m\rangle c_m - \beta c_n = 0$$

$$\frac{\partial F}{\partial c_n} = \text{c.c. of above.}$$

$$\frac{\partial F}{\partial \beta} = 0 \quad \Rightarrow \quad \sum_{n=1}^{N} |c_n|^2 = 1.$$

We see that β is the eigenvalue of the truncated matrix $N \times N$ of H in the basis $\{|n\rangle\}$, and $\{c_n\}$ are the normalized eigenvectors. The minimum eigenvalue β is rigorously an upper bound to E_0.

Notice in the proof of the variational upper bound thm,

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if we think of the ket $|\varepsilon\rangle$ as a small correction to the ground state wave fn $|0\rangle$ (hence the notation), then the error in the energy, namely $\langle\varepsilon|$ [illegible] $(H-E_0)|\varepsilon\rangle$, is $O(\varepsilon^2)$. Thus, the error in the energy is of higher order than the error in the wave fn. Often rather crude guesses as to the ground state wave fn will give rather good estimates of the energy.

In general, the variational method ~~gives~~ does not allow one to impose rigorous bounds (upper or lower) on the excited state energies (only the upper bound on the ground state). If the ground state wave fn. were known exactly, you could use trial wave fns that were exactly orthog. to it, and get a rigorous upper bound to E_1. But the gnd state wave fn is usually not known exactly.

If the Hamiltonian has exact symmetries (e.g., rotations, parity, ...) then you can get rigorous upper bounds to the minimum energy state in each symmetry class, by using trial wave fns. that have the given symmetry.

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Now we consider identical particles. As an example, consider two identical particles interacting by means of a central force potential,

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + V(|\vec{r}_2 - \vec{r}_1|).$$

The masses are equal because the particles are identical. This could be the rotation-vibration Hamiltonian for a homonuclear diatomic molecule, e.g. H_2, N_2, O_2 (but the nuclear isotopes must be identical).

A new type of symmetry operation arises in such a Hamiltonian, namely exchange. We denote the operator that exchanges particles 1 and 2 by E_{12}. Its precise definition will be given in a moment, but it's easy to see that H is invariant if we swap labels 1 and 2. Thus, we can believe that we will have

$$E_{12}\, H\, E_{12}^{\dagger} = H,$$

so H and E_{12} will possess simultaneous eigenstates.

Now to make a precise definition of E_{12}. Let $\mathcal{E}$ be the Hilbert space of a single particle. Then the total Hilbert space for the 2-particle system is $\mathcal{E}_{tot} = \mathcal{E} \otimes \mathcal{E}$. We can

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regard this as the product of two identical copies of $\mathcal{E}$. In a product like this, we will always understand that the first factor refers to "particle 1" and the second to "particle 2", but if we wish to make this especially clear we will add particle labels in parentheses,

$$\mathcal{E}_{tot} = \mathcal{E}^{(1)} \otimes \mathcal{E}^{(2)} .$$

Let $\{|\alpha\rangle\}$ be a basis in $\mathcal{E}$, where α is ~~perhaps~~ one or more indices labelling basis states. Then a basis in $\mathcal{E}_{tot}$ is

$$\{ |\alpha\rangle^{(1)} \otimes |\beta\rangle^{(2)} \equiv |\alpha\beta\rangle \}$$

where $|\alpha\beta\rangle$ is shorthand for the product basis. The indices α, β take on the same values. Then we define E_{12} by

$$E_{12} |\alpha\beta\rangle = |\beta\alpha\rangle ,$$

or, more explicitly,

$$E_{12} \left(|\alpha\rangle^{(1)} \otimes |\beta\rangle^{(2)} \right) = \left(|\beta\rangle^{(1)} \otimes |\alpha\rangle^{(2)} \right).$$

This defines the action of E_{12} on a basis in $\mathcal{E}_{tot}$, but by linearity the definition is extended to arbitrary states in $\mathcal{E}_{tot}$.

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Note: It follows from this definition that E_{12} is Hermitian,

$$E_{12} = E_{12}^{\dagger},$$

and also

$$E_{12}^{2} = 1,$$

so E_{12} is also unitary,

$$E_{12}^{-1} = E_{12} = E_{12}^{\dagger}.$$

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Now let us see what E_{12} does in wave fn. language. Start with the case of spinless particles. We can take the basis in $\mathcal{E}$ to be $\{|\vec{r}\rangle\}$, the position eigenkets. Then the basis in $\mathcal{E}_{tot}$ is

$$\{ |\vec{r}_1\rangle^{(1)} \otimes |\vec{r}_2\rangle^{(2)} \equiv |\vec{r}_1 \vec{r}_2\rangle \},$$

and the 2-particle wave fn is

$$\Psi(\vec{r}_1,\vec{r}_2) = \langle \vec{r}_1 \vec{r}_2 | \Psi \rangle,$$

where $|\Psi\rangle$ is the state of the system. Note: the subscripts on $\vec{r}_1$ and $\vec{r}_2$ are not particle labels, they just label 2 points in space (that is, two basis vectors in the $\{|\vec{r}\rangle\}$ basis).

Now what is the wave fn. of the state $E_{12}|\Psi\rangle$? It is

$$\langle \vec{r}_1 \vec{r}_2 | \overset{\curvearrowleft}{E_{12}} | \Psi \rangle = \langle \vec{r}_2 \vec{r}_1 | \Psi \rangle = \Psi(\vec{r}_2,\vec{r}_1).$$

This is a simple rule:

$$\Psi(\vec{r}_1,\vec{r}_2) \xrightarrow{E_{12}} \Psi(\vec{r}_2,\vec{r}_1).$$

Next take the case of particles with spin. Here the single particle Hilbert space is $\mathcal{E} = \mathcal{E}_{orb} \otimes \mathcal{E}_{spin}$ with basis $\{ |\vec{r} m\rangle = |\vec{r}\rangle \otimes |m\rangle \}$. So, the basis in $\mathcal{E}_{tot}$ is

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$$\{\,|\vec{r}_1 m_1\rangle^{(1)} \otimes |\vec{r}_2 m_2\rangle^{(2)} \equiv |\vec{r}_1\vec{r}_2 m_1 m_2\rangle\}.$$

Again, the 1 and 2 on $\vec{r}_1, \vec{r}_2, m_1, m_2$ do <u>not</u> label particles. Suppose we define the 2-particle wave fn by

$$\Psi_{m_1 m_2}(\vec{r}_1, \vec{r}_2) = \langle \vec{r}_1 \vec{r}_2 m_1 m_2 | \Psi \rangle .$$

Then since

$$E_{12}|\vec{r}_1\vec{r}_2 m_1 m_2\rangle = |\vec{r}_2\vec{r}_1 m_2 m_1\rangle,$$

we have

$$\Psi_{m_1 m_2}(\vec{r}_1, \vec{r}_2) \xrightarrow{E_{12}} \Psi_{m_2 m_1}(\vec{r}_2, \vec{r}_1).$$

The operator E_{12} exchanges both spin and spatial coordinates.

Now return to the central force Hamiltonian, and take the case of 2 spin 0 particles. An example is $^{16}O_2$ (the O_2 molecule with ^{16}O nucleus, which has spin 0). Then the total wave fn is

$$\Psi(\vec{r}_1, \vec{r}_2) = \text{lab frame wave fn.}$$

As usual in central force problems, we can go from lab to CM and relative variables:

$$\vec{R} = \frac{\vec{r}_1 + \vec{r}_2}{2}$$

$$\vec{r} = \vec{r}_2 - \vec{r}_1$$

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and then we transform Ψ to the new coordinates,

$$\Psi(\vec{r}_1,\vec{r}_2) = \Psi(\vec{R},\vec{r})$$

The Schrödinger eqn. ~~becomes~~ is separable in the new coords, that is, the Hamiltonian becomes

$$H = \frac{P^2}{2M} + \frac{p^2}{2\mu} + V(r)$$

where $\vec{P}$ and $\vec{p}$ are conjugate to $\vec{R}$ and $\vec{r}$. Thus, the Sch. eqn. $H\Psi = E\Psi$ possesses sol'ns in the form $\Phi(\vec{R})\,\psi(\vec{r})$. Such product functions form a basis in the space $\mathcal{E}_{CM}\otimes\mathcal{E}_{rel}$ which is another way of writing the 2-particle Hilbert space,

$$\mathcal{E}_{tot} = \mathcal{E}^{(1)}\otimes\mathcal{E}^{(2)} = \mathcal{E}_{CM}\otimes\mathcal{E}_{rel}.$$

Under E_{12}, the operators $\vec{R}$ and $\vec{r}$ transform according to

$$\vec{R} = \frac{\vec{r}_1+\vec{r}_2}{2} \longrightarrow \vec{R}$$

$$\vec{r} = \vec{r}_2-\vec{r}_1 \longrightarrow -\vec{r}.$$

Thus the 2-particle wave fn. in $(\vec{R},\vec{r})$ form transforms under exchange as

$$\Psi(\vec{R},\vec{r}) \xrightarrow{E_{12}} \Psi(\vec{R},-\vec{r}).$$

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Exchange behaves like parity as far as the relative coordinates are concerned, but it is not parity because π would also change the sign of $\vec{R}$. Be careful not to confuse E_{12} with π.

In the case of a product wave fn, exchange E_{12} affects only the relative part,

$$\Phi(\vec{R})\,\psi(\vec{r}) \xrightarrow{E_{12}} \Phi(\vec{R})\,\psi(-\vec{r}).$$