Variational Aspects of the Schrödinger Equation. [Ref. Davydov, ¶51.]

1) In the Lagrangian formulation of classical mechanics, the equations-of-motion are derived from a "minimum action principle". Recall that one defines...

$$\left.\begin{array}{l} \underline{\text{LAGRANGIAN}}: \; L = T - V = L(q_k, \dot{q}_k, t) \;\; \Big[q_k = \text{generalized cds, and: } \dot{q}_k = dq_k/dt; \\ \underline{\text{ACTION}}: \; I = \int_{t_1}^{t_2} L\,dt, \text{ on path } q_k(t_1) \to q_k(t_2). \end{array}\right\} \quad (1)$$

Then Hamilton's minimum action principle: $\delta I = 0$ (w.r.t. variations δq_k which vanish at endpoints of path: $\delta q_k(t_1) = \delta q_k(t_2) = 0$), generates the Euler-Lagrange eqtns-of-motion:★

$$\boxed{\partial L/\partial q_k - \frac{d}{dt}(\partial L/\partial \dot{q}_k) = 0}, \quad k = 1, 2, \ldots, k_{max} = \text{system \# degrees of freedom.} \quad (2)$$

Newton's 2nd law is included here, as -- for the 1D case...

$$L = \tfrac{1}{2}m\dot{q}^2 - V(q), \qquad \Big\| \quad \text{Euler-Lagrange}: \; \frac{d}{dt}(\partial L/\partial \dot{q}) = \partial L/\partial q$$

$$\text{so } \frac{\partial L}{\partial q} = -\frac{\partial V}{\partial q}, \quad \frac{\partial L}{\partial \dot{q}} = m\dot{q} \qquad \Big\| \quad \Rightarrow m\ddot{q} = -\partial V/\partial q = F, \text{ Newton II.} \quad (3)$$

The Lagrangian approach to mechanics is extremely useful in dealing with systems that move under constraints... the constraining forces can be cleverly eliminated.

★ Details of the variational calculation leading to Eqs. (2) are...

$$\delta I = \delta \int_{t_1}^{t_2} L(q_k, \dot{q}_k, t)\,dt = \int_{t_1}^{t_2} \sum_k \left[(\partial L/\partial q_k)\,\delta q_k + (\partial L/\partial \dot{q}_k)\,\delta \dot{q}_k \right] dt.$$

But: $\delta \dot{q}_k = \frac{d}{dt}\delta q_k$. Integrate the 2nd term in the integral by parts...

$$\int_{t_1}^{t_2} (\partial L/\partial \dot{q}_k)\,\delta \dot{q}_k\,dt = \int_{t_1}^{t_2} (\partial L/\partial \dot{q}_k)\,d\delta q_k = \left(\frac{\partial L}{\partial \dot{q}_k}\right)\delta q_k \Big|_{t_1}^{t_2} - \int_{t_1}^{t_2} \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_k}\right)\delta q_k\,dt$$

$$\text{so } \delta I = \sum_k \int_{t_1}^{t_2} \left[\frac{\partial L}{\partial q_k} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_k}\right) \right] \delta q_k\,dt = 0 \Rightarrow \underline{\underline{\left[\frac{\partial L}{\partial q_k} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_k}\right) \right] = 0}} \;\; \Big[\text{for arbitrary (independent) variations } \delta q_k$$

2) A "minimum-action" formulation is also possible for QM. Start by looking at the total system energy for the Schrödinger Hamiltonian...

$$\rightarrow \langle \mathcal{H} \rangle = \int \psi^* \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi\, d^3x \quad \int \text{for particle of mass } m \text{ in a potential } V(\vec{r}). \qquad \text{(4)}$$

Assume ψ & $\vec{\nabla}\psi$ vanish at ∞ (OK for <u>bound</u> systems) and partial-integrate:

$$\int_\infty \psi^* \nabla^2 \psi\, d^3x = \cancelto{0}{\oint_\infty (\psi^* \vec{\nabla}\psi)\cdot d\vec{S}} - \int_\infty (\vec{\nabla}\psi^*)\cdot(\vec{\nabla}\psi)\, d^3x$$

Soy $\langle \mathcal{H} \rangle = \int_\infty d^3x \left[(\hbar^2/2m)(\vec{\nabla}\psi^*)\cdot(\vec{\nabla}\psi) + V(\vec{r})\psi^*\psi\right]$

$$\xrightarrow{\text{or}/\!/} \langle \mathcal{H} \rangle = \int_{-\infty}^{\infty} dx \left[\frac{\hbar^2}{2m}\left(\frac{\partial\psi^*}{\partial x}\right)\left(\frac{\partial\psi}{\partial x}\right) + V(x)\psi^*\psi\right], \text{ in 1D} \qquad \text{(5)}$$

We claim that the manifestation of "minimum action" in this problem is that the system will seek and find a state of <u>minimum energy</u>, consistent with appropriate constraints on the wavefcn ψ. Thus we declare:

QM obeys a minimum energy principle: the admissible wavefcns ψ (for a bound-state problem) render $\delta\langle\mathcal{H}\rangle = 0$, subject to $\int \psi^*\psi\, dx = \text{cnst.}$

(6)

We can now show that this statement is equivalent to Schrödinger's Eqtn (for $\mathcal{H}$ in Eq.(5)), just as Hamilton's principle $\delta I = 0$ is equivalent to Newton II.

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3) To put the constraint in the QM problem, use a Lagrangian multiplier λ...

$$\left[\begin{array}{l} \text{Define: } \int F\,dx = \langle\mathcal{H}\rangle - \lambda \int \psi^*\psi\, dx, \quad \text{use } \langle\mathcal{H}\rangle \text{ of Eq.(5)} \\ \text{Soy } F(\psi, \psi^*; \psi', \psi^{*\prime}; x) = \frac{\hbar^2}{2m}\psi^{*\prime}\psi' + V(x)\psi^*\psi - \lambda\psi^*\psi. \end{array}\right\} \quad \text{(7)}$$

Consider ψ & ψ^* to be the independent generalized coordinates for the problem (like the q_k in Eq.(1)). The variational problem is:

V.A.S. Eq.

Min energy $\longleftrightarrow$ $\delta\int F\,dx = 0$, w.r.t. variations in ψ & ψ^*.

This implies two Euler-Lagrange Eqtns, viz...

$$\left.\begin{aligned} &\frac{\partial F}{\partial\psi} - \frac{d}{dx}\left(\frac{\partial F}{\partial\psi'}\right) = V\psi^* - \lambda\psi^* - \frac{\hbar^2}{2m}\frac{d}{dx}\psi^{*\prime} = 0, \\ &\frac{\partial F}{\partial\psi^*} - \frac{d}{dx}\left(\frac{\partial F}{\partial\psi^{*\prime}}\right) = V\psi - \lambda\psi - \frac{\hbar^2}{2m}\frac{d}{dx}\psi' = 0, \quad \text{w/}\ \psi' = \frac{d\psi}{dx}; \end{aligned}\right\} \quad (8)$$

i.e.

$$\longrightarrow -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = \lambda\psi, \text{ and complex conjugate equation.} \qquad (9)$$

Identify $\lambda = \langle\mathcal{H}\rangle = E$ as the total system energy. Then we can say for the Schrödinger problem:

$$\longrightarrow \left[\begin{aligned} &\delta\langle\mathcal{H}\rangle = 0, \text{ with: } \mathcal{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x), \text{ and the constraint } \int\psi^*\psi\,dx = 1, \\ &\text{is equivalent to the bound-state Schrödinger problem: } \mathcal{H}\psi = E\psi. \end{aligned}\right. \qquad (10)$$

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4) This sort of relation between a variational problem and an equivalent differential equation is <u>not restricted</u> to $\langle\mathcal{H}\rangle$ and the Schrödinger equation. In fact every variational (extremum) problem is connected with an eigenvalue equation, as we shall now show. We consider the following problem...

$$\left[\begin{aligned} &\text{For a general Hermitian operator } Q, \text{ find } \psi \text{ such that } \delta\langle Q\rangle = 0 \\ &(\text{w/ } \langle Q\rangle = \int\psi^* Q\psi\,dx), \text{ subject to the constraint: } \int\psi^*\psi\,dx = \text{cnst.} \end{aligned}\right] \qquad (11)$$

The variational statement is -- with μ = a real Lagrange multiplier...

$$\delta\left(\langle\psi|Q|\psi\rangle - \mu\langle\psi|\psi\rangle\right) = 0,$$

or/

$$\langle\overset{\text{vary }\psi^*}{\delta\psi}|\underset{\text{to right}}{Q|\psi}\rangle + \langle\underset{\text{to left}}{\psi|Q}|\overset{\text{vary }\psi}{\delta\psi}\rangle - \mu\left(\langle\delta\psi|\psi\rangle + \langle\psi|\delta\psi\rangle\right) = 0,$$

i.e.,

$$\longrightarrow \langle\delta\psi|(Q-\mu)\psi\rangle + \langle(Q-\mu)\psi|\delta\psi\rangle = 0. \qquad (12)$$

An explicit statement of Eq. (12) in configuration space is...

$$\rightarrow \int [(Q-\mu)\psi]\,\delta\psi^*\,dx + \int [(Q^*-\mu)\psi^*]\,\delta\psi\,dx = 0. \tag{13}$$

Now the variation $\delta\psi$ is arbitrary: we can choose $\delta\psi$ to be real or imaginary. So...

Choose $\delta\psi$ real: $\delta\psi^* = +\delta\psi$. Then Eq. (13) $\Rightarrow$

$$\int [(Q-\mu)\psi + (Q^*-\mu)\psi^*]\,\delta\psi\,dx = 0, \text{ so } \underline{(Q-\mu)\psi + (Q^*-\mu)\psi^* = 0}. \tag{14a}$$

Choose $\delta\psi$ imaginary: $\delta\psi^* = (-)\,\delta\psi$. Then Eq. (13) $\Rightarrow$

$$\int [-(Q-\mu)\psi + (Q^*-\mu)\psi^*]\,\delta\psi\,dx = 0, \text{ so } \underline{(Q-\mu)\psi - (Q^*-\mu)\psi^* = 0}. \tag{14b}$$

By adding & subtracting Eqs. (14a) & (14b), we have an eigenvalue eqtn for Q...

$$\left.\begin{matrix}(Q-\mu)\psi = 0\\ \text{\&}\ (Q^*-\mu)\psi^* = 0\end{matrix}\right\}\ \text{i.e.}\ \boxed{Q\psi = \mu\psi},\ \text{w/}\ \mu = \langle Q\rangle = \int \psi^* Q\psi\,dx = \text{cnst.} \tag{15}$$

SO

$\rightarrow$ $\delta\langle Q\rangle = 0$, with $\langle Q\rangle = \langle\psi|Q|\psi\rangle$ and the constraint $\langle\psi|\psi\rangle = 0$, is equi-

$\rightarrow$ valent to the eigenvalue problem: $Q\psi = \mu\psi$, w/ $\mu = \langle Q\rangle$, the eigenvalues of Q; ψ the corresponding eigenfcns. (16)

The statement in Eq. (10) re Schrodinger's problem (viz. $\delta\langle\mathcal{H}\rangle = 0$ and $\int\psi^*\psi\,dx = 1$ implying $\mathcal{H}\psi = E\psi$) is just one example of this general result.

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5) The condition $\delta\langle\mathcal{H}\rangle = 0$, equivalent to Schrödinger's Eqtn, ensures an extremum in the QM system energy, but not necessarily a minimum energy. However, there is an absolute minimum in the bound-state problem, namely the ground state energy, and we can look at how $\delta\langle\mathcal{H}\rangle = 0$ works for the ground state. We shall now show that the ground state energy can be approximated to arbitrarily high precision by judicious choice of a "trial wavefcn" ϕ which need not even be a solution to Schrodinger's Eqtn. This is as close as you will come to a free lunch in QM.

Consider : $\mathcal{H}\psi_n = E_n\psi_n$, w/ eigenfcns ψ_n & eigenvalues E_n not known.

Assume $\begin{cases} \text{existence of a ground state } \psi_0 \text{, with } \mathcal{H}\psi_0 = E_0\psi_0, \\ \text{and } E_0 \text{ is a lower bound on the energies} : E_0 \leq \text{all other } E_n. \end{cases}$

The true ground state energy is : $E_0 = \langle\psi_0|\mathcal{H}|\psi_0\rangle / \langle\psi_0|\psi_0\rangle$. (17)

For a sufficiently complicated $\mathcal{H}$, it may not be possible to even calculate ψ_0. So we make a guess ... i.e. we invent a "trial wavefcn" $\phi \sim \psi_0$ which has some resemblance to what we think ψ_0 should look like. Now, with $\mathcal{H}$ given, we can calculate an energy : $E = \langle\phi|\mathcal{H}|\phi\rangle / \langle\phi|\phi\rangle$. Question : how do E & E_0 compare?

We can show that no matter what ϕ is chosen, it is always true that $E \geq E_0$, with equality holding only if -- by accident -- we choose ϕ = true ψ_0. Then, by "improving" ϕ, i.e. modifying ϕ to drive E down to a minimum, we will always approach E_0 from above, i.e. $E \to E_0+$. We will never overshoot E_0.

Proof goes as follows. Even though we don't know the $\{\psi_n\}$, we do know that as eigenfcns of a Hermitian $\mathcal{H}$ they will form a complete set. So for any trial ϕ:

$\phi = \sum_n a_n\psi_n$, and : $\langle\phi|\phi\rangle = \sum_n |a_n|^2$, $\langle\phi|\mathcal{H}|\phi\rangle = \sum_n |a_n|^2 E_n$;

So/ trial energy : $E = \langle\phi|\mathcal{H}|\phi\rangle / \langle\phi|\phi\rangle = \sum_n E_n|a_n|^2 / \sum_n |a_n|^2$. (18)

BUT : $E_n \geq E_0 \Rightarrow \sum_n E_n|a_n|^2 \geq E_0 \sum_n |a_n|^2$, and : $\boxed{E \geq E_0}$. (19)

So/ $\boxed{E = \langle\phi|\mathcal{H}|\phi\rangle / \langle\phi|\phi\rangle \text{ gives an upper bound on the ground state energy } E_0\text{, i.e. } E \geq E_0\text{, for any trial wavefunction } \phi.}$ (20)

This is rather remarkable ... any ϕ will do as a starter, and with "improvement", E will more closely approach E_0. What's important about $E \geq E_0$ is that it guarantees no matter how you tinker with ϕ, you will never overshoot E_0 an go wandering off to energies $E < E_0$ w/o limit.

6) A way of fully exploiting the result of Eq. (20) is to parametrize the trial fcn ϕ:

$\phi = \phi(\alpha, \beta, \gamma, \ldots; x)$, parameters $\alpha, \beta, \gamma, \ldots$ (scale lengths, etc.) allow $\phi \sim \psi_0$;

so// $E = \langle\phi|\mathcal{H}|\phi\rangle / \langle\phi|\phi\rangle = E(\alpha, \beta, \gamma, \ldots)$, a fcn of the parameters,

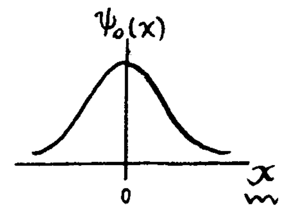
and// any value of E exceeds the ground state energy E_0;

in particular, the minimum value of $E(\alpha, \beta, \gamma, \ldots) \geqslant E_0$. (21)

So/ Minimize E by imposing: $\frac{\partial E}{\partial \alpha} = \frac{\partial E}{\partial \beta} = \frac{\partial E}{\partial \gamma} = \cdots = 0$.

then// $E(\alpha, \beta, \ldots)\Big|_{\partial E/\partial\alpha = 0,\, \partial E/\partial\beta = 0, \ldots} \geqslant 0$ is the best upper bound to E_0 that can be calculated with the trial wavefunction $\phi(\alpha, \beta, \ldots; x)$.

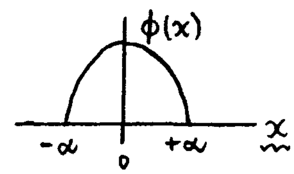
EXAMPLE Ground state of the SHO.



for 1D SHO: $\mathcal{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$. (22)

We know that the ground state wavefcn $\psi_0(x)$ looks like the sketch (actually $\psi_0(x) \propto \exp[-(\text{cnst})x^2]$) and that the ground state energy $E_0 = \frac{1}{2}\hbar\omega$. But, w/o bothering to solve $\mathcal{H}\psi = E\psi$, construct a (crude) trial fcn ϕ by...

$$\rightarrow \phi(x) = \begin{cases} A(\alpha^2 - x^2), & \text{for } |x| \leqslant \alpha, \\ 0, & \text{for } |x| > \alpha; \ \alpha = \text{free parameter}. \end{cases} \tag{23}$$



so// $$\langle\phi|\phi\rangle = A^2 \int_{-\alpha}^{+\alpha} (\alpha^2 - x^2)^2\, dx = \frac{16}{15}A^2\alpha^5 \tag{24a}$$

and// $$\langle\phi|\mathcal{H}|\phi\rangle = A^2 \int_{-\alpha}^{+\alpha} (\alpha^2 - x^2)\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2\right](\alpha^2 - x^2)\, dx$$

$$= A^2 \left\{ \frac{\hbar^2}{m} \underbrace{\int_{-\alpha}^{\alpha} (\alpha^2 - x^2)\, dx}_{(4/3)\alpha^3} + \frac{1}{2}m\omega^2 \underbrace{\int_{-\alpha}^{\alpha} x^2(\alpha^2 - x^2)^2\, dx}_{(16/105)\alpha^7} \right\} \tag{24b}$$

then// $$\longrightarrow E(\alpha) = \langle\phi|\mathcal{H}|\phi\rangle / \langle\phi|\phi\rangle = \frac{5}{4}\left(\frac{\hbar^2}{m\alpha^2}\right) + \frac{1}{14}m\omega^2\alpha^2. \tag{24c}$$

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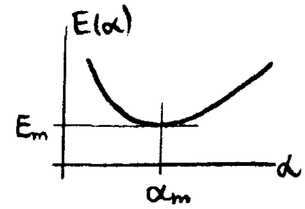

The trial energy $E(\alpha)$ calculated in Eq. (24c) exceeds the ground state energy E_0 for all values of α (i.e. all forms of ϕ). So we can minimize $E(\alpha)$ w.r.t. α and still stay above E_0. Thus...

$$\left[\begin{array}{l} \text{Minimization}: \ \partial E/\partial\alpha = 0 \Rightarrow \alpha^2 = \sqrt{\frac{35}{2}}\,(\hbar/m\omega) = \alpha_m^2; \\ \text{and}\ \ E(\alpha_m) = \sqrt{\frac{10}{7}} \times \frac{1}{2}\hbar\omega = \underline{\underline{1.195\,E_0 = E_m}}. \end{array}\right. \tag{25}$$

So we fall just 20% above the actual energy E_0. A big improvement can be had by tinkering ϕ to: $\phi(x) = A(\alpha^2 - x^2)^2$ for $|x| \leq \alpha$; $\phi(x) = 0$, for $|x| > \alpha$. Then: $E(\alpha) = \frac{3}{2}(\hbar^2/m\alpha^2) + \frac{1}{22}m\omega^2\alpha^2$, and $E_{min} = \sqrt{\frac{12}{11}} \times \frac{1}{2}\hbar\omega = \underline{\underline{1.045\,E_0}}$. The interested student should try this calculation as an exercise.

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7) The variational method can -- with increasing difficulty -- be extended to estimates of the excited state energies $E_1, E_2, \ldots$ lying above the ground state E_0. What we have done for the ground state is (symbolically):

$$\rightarrow E_0^{(est.)} = \min.\langle\phi_0|\mathcal{H}|\phi_0\rangle \geq E_0, \ \text{w/}\ \langle\phi_0|\phi_0\rangle = 1; \ \phi_0 = \text{trial wavefcn}. \tag{26}$$

Here we have normalized ϕ_0 a priori. For the first excited state E_1, we construct a trial wavefcn ϕ_1 which is orthogonal to ϕ_0, i.e. $\langle\phi_1|\phi_0\rangle = 0$, thus mimicking the required orthogonality of the true eigenfcns ψ_n. Then

$$\rightarrow E_1^{(est.)} = \min.\langle\phi_1|\mathcal{H}|\phi_1\rangle \geq E_1, \ \text{w/}\ \langle\phi_1|\phi_1\rangle = 1 \ \underline{\underline{\text{and}}}\ \langle\phi_1|\phi_0\rangle = 0. \tag{27}$$

That $E_1^{(est)} \geq E_1$ can be shown by the sort of calculation in Eqs. (18)-(20) above, starting from $\phi_1 = \sum_{n=1}^{\infty} b_n\psi_n$ (no ψ_0 present)... see Davydov ¶ 51. Similarly, by constructing $\phi_2 \perp \phi_1$ and ϕ_0, we can get $E_2^{(est)} \geq E_2$, etc. In general...

$$\rightarrow E_n^{(est.)} = \min\langle\phi_n|\mathcal{H}|\phi_n\rangle \geq E_n, \ \text{w/}\langle\phi_n|\phi_n\rangle = 1 \ \underline{\underline{\text{and}}}\ \langle\phi_n|\phi_k\rangle = 0 \ \big\}\, k = 0, 1, \ldots, n-1 \tag{28}$$

The accumulating # of orthogonality conditions soon makes this method unwieldy.