Program for finding Schrödinger's Eqtn w/ external forces.

The Schrödinger Equation with External Forces

We shall derive Schrödinger's Wave Eqtn for the wavefcn $\Psi(\mathbf{r},t)$ of a QM particle of mass m moving in the presence of external forces. Program is:

- start from a generalized version of the free particle wave eqtn for Ψ;
- use packet solutions for the wave fcn Ψ;
- define particle (packet) motion via expectation values;
- impose condition that the particle's motion obeys the Correspondence Principle, in the sense that -- on average -- m moves per Newton's Laws.

(37)

---

1) We work in 1D for simplicity (generalization to 3D is ~obvious). Write a generalization of Schrödinger's free particle eqtn...

$$\rightarrow i\hbar\frac{\partial}{\partial t}\psi(x,t) = \mathcal{H}\,\psi(x,t), \quad \text{w/ } \mathcal{H} = \frac{1}{2m}p^2 + Q,$$

where: $p = -i\hbar\,\partial/\partial x$, per Eq. (36) above;

and : $Q = Q(x,p;t)$, due to external forces, is to be found. (38)

For free particles, $Q \equiv 0$, and: $i\hbar\frac{\partial}{\partial t}\psi = -\frac{\hbar^2}{2m}(\partial^2/\partial x^2)\psi$. Ultimately, we will show that Q = potential energy V associated with the external forces.

Now, w.r.t. packet-type solutions to Eq. (38), define m's momentum by

$$\rightarrow \langle p\rangle = m\frac{d}{dt}\langle x\rangle, \quad \langle\ \rangle \Rightarrow \text{expectation value w.r.t. } \psi. \qquad (39)$$

This is a Correspondence Principle-type statement... on average, the particle's momentum will correspond to the Newtonian form: $p = m\frac{d}{dt}x$. The definition of m's momentum per Eq. (39) will impose a restriction on our to-be-found Q... viz. Q is real: $Q^* = Q$. Now we show that.

<u>Restriction on Q via definition: $\langle p \rangle = m(d/dt)\langle x \rangle$.</u>

In Eq. (39), calculate (all $\int = \int_{-\infty}^{\infty}$)...

$$\rightarrow \frac{d}{dt}\langle x \rangle = \frac{d}{dt}\int \psi^*\{x\}\psi\, dx = \int\left[\overset{2}{\left(\frac{\partial \psi^*}{\partial t}\right)} x\psi + \psi^* x \overset{1}{\left(\frac{\partial \psi}{\partial t}\right)}\right]dx; \quad (40)$$

but// 1: $\dfrac{\partial \psi}{\partial t} = -\dfrac{i}{\hbar}\left[-\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2} + Q\right]\psi$, and// 2: $\dfrac{\partial \psi^*}{\partial t} = +\dfrac{i}{\hbar}\left[-\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2} + Q^*\right]\psi^*$,

so//

$$\left.\begin{aligned} &\frac{d}{dt}\langle x \rangle = \frac{i\hbar}{2m}\int\left[\psi^* x\left(\frac{\partial^2 \psi}{\partial x^2}\right) - \left(\frac{\partial^2 \psi^*}{\partial x^2}\right)x\psi\right]dx + \mathcal{V}, \\ &\text{where}: \ \mathcal{V} = \frac{i}{\hbar}\int (Q^* - Q)\psi^* x \psi\, dx. \end{aligned}\right\} \quad (41)$$

This improbable-looking mess must be made to fit the definition in Eq. (39), viz: $\frac{d}{dt}\langle x \rangle = \frac{1}{m}\langle p \rangle = \frac{1}{m}\int \psi^*\{-i\hbar\,\partial/\partial x\}\psi\, dx$. Evidently, we must simplify (41). We do that by twice partial-integrating the second term RHS in (41), imposing that ψ & $\partial\psi/\partial x$ vanish at ∞...

$$\rightarrow \int\left(\frac{\partial^2 \psi^*}{\partial x^2}\right)x\psi\, dx = \int\left[d\left(\frac{\partial \psi^*}{\partial x}\right)\right]x\psi\, dx = \underbrace{\left(\frac{\partial \psi^*}{\partial x}\right)x\psi\Big|_{-\infty}^{+\infty}}_{\rightarrow 0} - \int \frac{\partial \psi^*}{\partial x}\left[\frac{\partial}{\partial x}(x\psi)\right]dx$$

$$= -\int d\psi^* \frac{\partial}{\partial x}(x\psi)\, dx = \underbrace{-\psi^*\frac{\partial}{\partial x}(x\psi)\Big|_{-\infty}^{+\infty}}_{\rightarrow 0} + \int \psi^* \frac{\partial^2}{\partial x^2}(x\psi)\, dx$$

$$= +\int \psi^* \frac{\partial}{\partial x}\left(\psi + x\frac{\partial \psi}{\partial x}\right)dx = 2\int \psi^* \frac{\partial \psi}{\partial x}dx + \int \psi^* x \frac{\partial^2 \psi}{\partial x^2}dx. \quad (42)$$

From the last expression in (42), we can form the integral in (41), viz...

$$\rightarrow \int\left[\psi^* x\left(\frac{\partial^2 \psi}{\partial x^2}\right) - \left(\frac{\partial^2 \psi^*}{\partial x^2}\right)x\psi\right]dx = -2\int \psi^*\left(\frac{\partial \psi}{\partial x}\right)dx. \quad (43)$$

Use of this result in Eq. (41) allows us to write...

$$\rightarrow \frac{d}{dt}\langle x \rangle = \frac{1}{m}\int \psi^*\left\{-i\hbar\frac{\partial}{\partial x}\right\}\psi\, dx + \mathcal{V} = \frac{1}{m}\langle p \rangle + \mathcal{V};$$

so// if $\underline{\underline{\langle p \rangle = m\frac{d}{dt}\langle x \rangle}}$, then $\mathcal{V} = \frac{i}{\hbar}\int (Q^* - Q)\psi^* x\psi\, dx \equiv 0$,

for all ψ... possible only if $Q^* = Q$, i.e. <u>Q is real</u>. **QED.** (44)

Identification of Q = V (potential energy) by imposing F = ma.

2) Now we impose Newton II on the motion, i.e. $ma = F$, or $\frac{d}{dt}p = F$. Since we are working with expectation values, we need to calculate...

$$\rightarrow \frac{d}{dt}\langle p\rangle = -i\hbar\frac{d}{dt}\int\psi^*\frac{\partial\psi}{\partial x}dx = -i\hbar\int\Big[\Big(\frac{\partial\psi^*}{\partial t}\Big)\frac{\partial\psi}{\partial x} + \psi^*\frac{\partial}{\partial x}\Big(\frac{\partial\psi}{\partial t}\Big)\Big]dx$$

put in S. Eq. per Eq. (38)

Q is real

$$= \int\Big\{\Big[-\frac{\hbar^2}{2m}\frac{\partial^2\psi^*}{\partial x^2} + Q\psi^*\Big]\frac{\partial\psi}{\partial x} - \psi^*\frac{\partial}{\partial x}\Big[-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + Q\psi\Big]\Big\}dx$$

$$= -\frac{\hbar^2}{2m}\int\Big[\Big(\frac{\partial^2\psi^*}{\partial x^2}\Big)\frac{\partial\psi}{\partial x} - \psi^*\frac{\partial}{\partial x}\Big(\frac{\partial^2\psi}{\partial x^2}\Big)\Big]dx - \int\psi^*\Big(\frac{\partial Q}{\partial x}\Big)\psi\,dx. \qquad (45)$$

by partial integrations

$$\psi^*\frac{\partial}{\partial x}\Big(\frac{\partial^2\psi}{\partial x^2}\Big) = -\Big(\frac{\partial\psi^*}{\partial x}\Big)\frac{\partial}{\partial x}\Big(\frac{\partial\psi}{\partial x}\Big) = +\Big(\frac{\partial^2\psi^*}{\partial x^2}\Big)\frac{\partial\psi}{\partial x} \Rightarrow$$ 1st integral RHS in Eq. (9) is $\equiv 0$.

so//
$$\underline{\underline{\frac{d}{dt}\langle p\rangle = \int\psi^*\Big\{-\frac{\partial Q}{\partial x}\Big\}\psi\,dx = \langle -\partial Q/\partial x\rangle.}} \qquad (46)$$

This result provides substantial information on what the "unknown" Q can be. Newton II can be written: $\frac{d}{dt}p = \underline{F = -\partial V/\partial x}$, where V is the potential fcn [$V = V(x,t)$ in general] from which the force F is derived. Comparison with (46) shows that: $\partial Q/\partial x = \partial V/\partial x$, in an expectation value sense, so that: <u>Q = V + space-independent cnst.</u> We take the cnst $\equiv 0$, since it would be uniform everywhere at a given time, and would just set a relative zero of energy. Thus we claim...

[if// $\frac{d}{dt}\underline{\underline{\langle p\rangle = \langle F\rangle}}$, then// $\underline{\underline{Q = V = \text{system potential energy}}}$. **QED** (47)

This is enough to establish the 1D Schrödinger Eqtn for a particle m in an external field as...

$$\boxed{i\hbar\frac{\partial}{\partial t}\psi = \mathcal{H}\psi, \text{ w/ } \mathcal{H} = \frac{p^2}{2m} + V} \quad \text{w/ } p = -i\hbar\,\partial/\partial x,\; V = \text{P.E. of field}. \qquad (48)$$

REMARKS On Schrödinger's external field wave eqtn, Eq.(48).

1. Generalization from 1D to 3D is simple...

$$\mathcal{H}(1D) = \frac{1}{2m}p^2 + V(x,t) \rightarrow \mathcal{H}(3D) = \frac{1}{2m}\mathbf{p}^2 + V(\mathbf{r},t), \text{ w/ } \mathbf{p} = -i\hbar\nabla;$$

so/ $$\boxed{i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r},t)\right]\psi(\mathbf{r},t)}$$ SCHRÖDINGER'S WAVE EQTN (in 3D, particle m in field). (49)

2. A continuity eqtn can be written for Eq.(49), just as for a free particle...

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi \quad \leftarrow \text{multiply on left by } \psi^*$$

and/

$$-i\hbar\frac{\partial\psi^*}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi^* + V\psi^* \leftarrow \text{multiply on left by } \psi$$

then subtract

$$\Longrightarrow i\hbar\left[\psi^*\left(\frac{\partial\psi}{\partial t}\right) + \left(\frac{\partial\psi^*}{\partial t}\right)\psi\right] = -\frac{\hbar^2}{2m}\left[\psi^*(\nabla^2\psi) - (\nabla^2\psi^*)\psi\right];$$

or/ $$\boxed{\frac{\partial\rho}{\partial t} + \nabla\cdot\mathbf{J} = 0}\ \surd$$ w/ probability density: $\rho = \psi^*\psi = |\psi|^2$; (50)

prob. current density: $\mathbf{J} = \frac{\hbar}{2im}\left[\psi^*(\nabla\psi) - (\nabla\psi^*)\psi\right]$.

3. The addition of the P.E. term in V in Eq.(49) has not affected the form of the continuity eqtn; ρ & $\mathbf{J}$ in (50) are the same form as in Eq.(19) for the free particle (only ψ will change its content when $V \neq 0$). As before, we get conservation of probability from the continuity eqtn...

$$\rightarrow \frac{\partial}{\partial t}\int_\infty \rho\, d^3r = \frac{\partial}{\partial t}\int_\infty |\psi|^2 d^3r = -\int_\infty \nabla\cdot\mathbf{J}\, d^3r = -\oint_\infty \mathbf{J}\cdot d\mathbf{S} \rightarrow 0, \quad (51)$$

for ψ & $\nabla\psi$ that vanish at ∞. Then: $\int_\infty |\psi|^2 d^3r$ = time indept. cnst = 1.

4. We note that $\mathcal{H}$ in Eq.(49) is the total system Hamiltonian (operator), since: $\langle\mathcal{H}\rangle = \langle \mathbf{p}^2/2m\rangle + \langle V\rangle$ = K.E. + P.E. = $\langle E\rangle$, total system energy (in an expectation value sense). Then, in the same expectation value sense...

$$\mathcal{H}\psi = i\hbar\frac{\partial}{\partial t}\psi \Rightarrow \langle\mathcal{H}\rangle = \langle E\rangle = \langle i\hbar\,\partial/\partial t\rangle, \text{ for exp. values w.r.t. } \psi;$$

so/ m's total energy $E \rightarrow E_{op} = i\hbar\,\partial/\partial t$, as suggested in Eq.(4), p. Sch. 2. (52)

Time-independent version of Schrödinger's Wave Eqtn.

3) For QM systems where the potential energy V is independent of time, a simplification of the Schrödinger Eqtn, Eq. (49) is possible. As follows...

Suppose $V = V(\mathbf{r})$ is time-indept. Let: $\psi(\mathbf{r},t) = u(\mathbf{r}) f(t)$.

Then: $i\hbar \frac{\partial \psi}{\partial t} = \left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi$, becomes a separable PDE, as:

$$\rightarrow \underbrace{\frac{i\hbar}{f}\cdot\frac{df}{dt}}_{\text{fcn of } t \text{ only}} = \underbrace{\frac{1}{u}\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)u}_{\text{fcn of } \mathbf{r} \text{ only}} = \underline{W}, \text{ a cnst indept. of } \mathbf{r} \,\&\, t.$$

... so: $(i\hbar/f)\,df/dt = W$ has solution: $f(t) = \overset{\text{arbitrary cnst}}{A}\, e^{-(i/\hbar)Wt}$...

and// $\psi(\mathbf{r},t) = A\,u(\mathbf{r}) \exp[-(i/\hbar)Wt]$, is a solⁿ for wavefcn ψ,

with// $\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)u(\mathbf{r}) = W\,u(\mathbf{r})$, W = separation cnst. (53)

We can choose the multiplicative cnst A in $f(t)$ to be $A=1$; then ψ & u have the same normalization, as: $\int_\infty |\psi|^2 d^3r = \int_\infty |u|^2 d^3r = 1$.

The significance of the separation cnst W in Eq. (53) is easily seen. Calculate:

$$\rightarrow \langle E\rangle = \int_\infty \psi^*(\mathbf{r},t)\left\{i\hbar\frac{\partial}{\partial t}\right\}\psi(\mathbf{r},t)\,d^3r = \int_\infty [u^*(\mathbf{r})e^{+\frac{i}{\hbar}Wt}]\, i\hbar\frac{\partial}{\partial t}[u(\mathbf{r})e^{-\frac{i}{\hbar}Wt}]\,d^3r$$

$$= \int u^*(\mathbf{r})\{W\}u(\mathbf{r})\,d^3r = \langle W\rangle, \text{ since } W = \text{cnst (indept. of } \mathbf{r} \,\&\, t);$$

So// $\underline{W = E = \text{total system energy}}$, cnst in time (i.e. $\frac{dW}{dt} = 0 \Rightarrow E = \text{cnst}$). (54)

Summarizing these results, we can state...

If the P.E. $V = V(\mathbf{r})$ is time-independent, then a particular solution to Schrödinger's Eqtn [Eq. (49)] is: $\psi(\mathbf{r},t) = u(\mathbf{r})\exp(-\frac{i}{\hbar}Et)$, w/ E is the (constant) total system energy ($E = \langle K.E. + P.E.\rangle$), and $u(\mathbf{r})$ obeys

$$\boxed{\left[-(\hbar^2/2m)\nabla^2 + V(\mathbf{r})\right]u(\mathbf{r}) = E\,u(\mathbf{r})}$$ TIME-INDEPT. SCHRÖDINGER EQ. (system energy E = constant). (55)

$u(\mathbf{r})$ is called a "stationary state solution."