Quantum Mechanics *H.T. 2001*

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Supplementary Problem Set

The problems in this set are things which are certainly not in the syllabus but you may find entertaining.

1. The Wigner Distribution (for Fourier transform fans)

   In classical mechanics, one way to describe the motion of a particle (or system of particles) is in terms of its position x and momentum p as a function of time (for 1-D, for simplicity). $x(t)$ and $p(t)$ trace out a curve in a 2-D plot of x versus p. Such "x-p" space is called "phase space". For example, suppose a particle of mass m is acted on by the SHO force $-m\omega^2\, x$.

   Let $x(0) = a$, $\dot{x}(0) = 0$. Show that the trajectory in x-p space is an ellipse.

   In quantum mechanics, we can't have states in which both x and p are well defined, so classical phase space doesn't exist. We can only talk about the behaviour in one of x or p at a time - or so it would seem. Wigner, however, came up with a "nice try" at having both x and p information at once. He defined [E.P.Wigner, Physical Review, 40 (1932) 749]:

$$W_\psi(x,p) = \frac{1}{\pi\hbar}\int_{-\infty}^{\infty} dy \quad e^{2ipy/\hbar}\psi^*(x+y)\psi(x-y).$$

   Show that
$$\int_{-\infty}^{\infty} W_\psi(x,p)dp = |\psi(x)|^2$$
   and that
$$\int_{-\infty}^{\infty} W_\psi(x,p)dx = |\psi(p)|^2$$
   where (as usual) $\psi(p)$ is the p- space amplitude obtained from ψ(x) by Fourier Transform. Why are these "nice properties"?

Evaluate $W_\psi(x,p)$ for the Gaussian wave packet $\psi(x) = \frac{1}{(\pi a^2)}\frac{1}{4}e^{\frac{-x^2}{2a^2}}e^{\frac{ip_0x}{\hbar}}$ and interpret it. Discuss the spread in x and the spread in p.

Everything seems OK; what could be the catch? Think about the answer before proceeding...

Suppose we consider now a superposition of two Gaussians:

$$\Psi = e^{-(x-x_1)^2/2a^2} + e^{-(x-x_2)^2/2a^2}$$

(forgetting the normalisation now).

It turns out that

$$W_\Psi \propto \frac{1}{2}(W_1 + W_2) + \frac{1}{\pi\hbar}e^{-\frac{p^2a^2}{\hbar^2}-\frac{x^2}{a^2}}\cos\left[\frac{(x_2-x_1)}{\hbar}p\right]$$

where W_1 is the W for $e^{(-x-x_1)^2/2a^2}$ and similarly for W_2.

Sketch W_Ψ [hints: W_1 and W_2 peak at $x = x_1$ and $x = x_2$ respectively, and both peak at $p = 0$; if x_1 and x_2 are a good deal bigger than a, the "tails" of the Gaussians will have fallen right off for x near zero; what about the $\cos[(x_2 - x_1)p/\hbar]$ term, which is modulated by exponential cut-offs in both x and p?]

[If you want to see it, it is Figure 5 in W.H.Zurek's article in Physics Today, October 1991, 36-44.] So what is the "snag" with W?

2. Gaussian wave packets: dispersion

i) A time-dependent free-particle (plane wave) solution of the 1-D Schrödinger equation is $\psi(x,t) = N\exp(ikx - iEt/\hbar)$ where N is a normalization constant and $E = p^2/2m = \hbar^2k^2/2m = \hbar\omega$. It follows that for these waves the frequency ω is *not* proportional to k but to k^2: $\omega = \hbar k^2/2m$. This makes a dramatic difference to the way a packet of these waves evolves with time: the packet does *not* maintain its shape, but "flattens out", a phenomenon called *dispersion* (of the packet). Consider the packet

$$\psi(x,t) = \frac{1}{2\Delta k}\int_{k_0-\Delta k}^{k_0+\Delta k} e^{ikx - i\hbar k^2 t/2m}dk$$

Note that $\psi(x,0)$ is just our simple time-independent packet from Set 3 Q.10. This time the integral can *not* be done in terms of elementary functions. However, if $k_0 \gg \Delta k$ and the t-term in the exponent is "not too big" we can expand "k^2" about the point $k = k_0$ by a Taylor series: $k^2 = k_0^2 + (k - k_0).2k_0$, and we are back to only a *linear* term in the exponent, which can be integrated exactly. Show that in this approximation

$$|\psi(x,t)|^2 = \frac{\sin^2[\Delta k(x - vt)]}{[\Delta k(x - vt)]^2}$$

where $v = \hbar k_0/m$, and describe how this packet moves as t varies.

(ii) To see the spreading explicitly, it is convenient to introduce a packet which *can* be integrated analytically, namely the "Gaussian packet"

$$\psi_G(x,t) = N \int_{-\infty}^{\infty} e^{-k^2/2(\Delta k)^2} e^{ikx - i\hbar k^2 t/2m} dk$$

where N is a normalization constant we shan't bother with. Here the "$(\Delta k)^2$" controls the exponential fall off of the "packet function" $\exp -k^2/2(\Delta k)^2$. The integral in ψ_G can be done by completing the square. Show that the integrand can be written as

$$e^{-a(t)^2 k'^2 - x^2/4a(t)^2}$$

where

$$a(t) = \left(\frac{1}{2(\Delta k)^2} + \frac{i\hbar t}{2m} \right)^{\frac{1}{2}}, \quad \text{and} \quad k' = k - \frac{ix}{2a(t)^2} \quad .$$

Using the result $\int_{-\infty}^{\infty} e^{-a^2 k'^2} dk' = \frac{\sqrt{\pi}}{a}$ (true for complex a also), we arrive at

$$\psi_G(x,t) = \frac{N\sqrt{\pi}}{a(t)} e^{-x^2/4a(t)^2} \quad .$$

So

$$|\psi_G(x,t)|^2 \propto \frac{1}{|\ a(t)\ |^2}\ e^{-x^2/2|a(t)|^2},$$

where

$$2|a(t)|^2 = \frac{1}{(\Delta k)^2} \left(1 + \frac{\hbar^2 t^2}{m^2} (\Delta k)^4 \right).$$

The important exponential term is

$$e^{-x^2/[\Delta x(t)]^2}$$

where

$$\Delta x(t) = \frac{1}{\Delta k}(1 + \frac{\hbar^2 t^2}{m^2}(\Delta k)^4)^{\frac{1}{2}}.$$

This shows clearly that this packet has a spread $\Delta x(t)$ *which increases with* t: It disperses. Indeed, for $\frac{\hbar^2 t^2 (\Delta k)^4}{m^2} \gg 1$, the spread increases linearly with t.

Show that the packet doubles in size (after $t = 0$) in a time $\sqrt{3} m\hbar/(\hbar \Delta k)^2$ and explain this in physical terms. Can you be more precise now, about what "not too big" meant in (ii)?

Suppose an electron is described by such a packet, and is confined at $t = 0$ to a region of size 10^{-10}m. How long will it take for the packet to spread to twice its size? How long will it take to fill a room?

Now consider a speck of dust weighing 10^{-6} kg of linear dimension 10^{-6}m, localized to a region of its own size. How long will it take for its localization to double (in years)?

3. Double Well Potential

A quantum particle is confined in a "*double well*" potential defined by

$$\begin{aligned} V &= \infty \text{ for } x < -a - b \\ &= 0 \text{ for } -a - b < x < -b \\ &= V_0 \text{ for } -b < x < b \\ &= 0 \text{ for } b < x < a + b \\ &= \infty \text{ for } x > a + b \end{aligned}$$

(i) Consider first the case $a \geq b$. *Without doing any calculations*, sketch the forms of the wavefunctions of the ground state and of the first excited state. [Hint: think about the wave-functions for the ground states in the separate wells in $-a-b < x < -b$ and in $b < x < a+b$, which are separated by the barrier V_0; these have to be joined together somehow across $-b < x < b$; the ground state of the double well is symmetric in $x \leftrightarrow -x$, the first excited state is antisymmetric (why?)].

What can you say about the energies of these two lowest-lying states?

(ii) Now consider b becoming smaller, tending eventually to zero (so that then the well becomes a single well of width $2a$). Describe how the two wavefunctions you have sketched in (i) "evolve" as b gets smaller. What are their forms when $b \to 0$, and what can you say about the way the two corresponding energy eigenvalues change (as a function of b) as $b \to 0$?

(iii) Now go back to the case $b \geq a$. Describe qualitatively the wavefunctions for the *next two* excited states. What can you say about their energies?

(iv) Now consider the case of a *series* of N potential wells, all separated by $b \geq a$. Describe qualitatively the energy levels of a particle in such a *periodic array* of wells.

[This is a useful model for a conduction electron, say, in a one-dimensional metal, with the wells representing the ion cores and the infinite walls at each end representing the edges of the metal. Your answer to (iv) should help you to understand the origin of *energy bands* in solids.]

4. The previous problem can be solved analytically as follows. Let the energy of a bound state be $E (E < V_0)$, and define

$$k = (2mE/\hbar^2)^{\frac{1}{2}}, \quad K = (2m(V_0 - E)/\hbar^2)^{\frac{1}{2}}$$

where m is the mass of the particle. First of all we note that parity is a good quantum number so that the energy eigenstates can be classified by parity. The even parity states have wavefunctions of the form

$$\begin{aligned} \psi_e(x) &= A \sin k(a + b - x) \quad \text{for} \quad b \leq x \leq a + b \\ &= B \cosh Kx \quad \text{for} \quad 0 \leq x \leq b \end{aligned}$$

with a symmetrical reflection about the origin, and the odd parity states have wavefunctions of the form

$$\begin{aligned} \psi_0(x) &= C \sin k(a + b - x) \quad \text{for} \quad b \leq x \leq a + b \\ &= D \sinh Kx \quad \text{for} \quad 0 \leq x \leq b \end{aligned}$$

with an antisymmetrical reflection about the origin.

(i) By applying the boundary conditions at $x = b$, show that the energy eigenvalues are given by the roots of

$$k \cot ka + K \tanh Kb = 0 \quad (I_+)$$

for the even-parity states, and by the roots of

$$k \cot ka + K \coth Kb = 0 \quad (I_-)$$

for the odd-parity states.

(ii) Consider the case $e^{-Kb} \ll 1$ (very little tunnelling across the barrier), and $V_0 \gg E$ (E well below the barrier height). Explain the resulting form of (I_+) and (I_-).

(iii) Consider the case $b \to 0$. What are the solutions (for k) of (I_+) and (I_-) in this case? Explain the results.

(iv) In general, (I_+) and (I_-) have to be solved numerically. For this it is convenient to put everything in dimensionless form. Let $ka = x$, $\left(\frac{2mV_0}{\hbar^2}\right)^{\frac{1}{2}} a = v$, and $b/a = r$. Show that (I_+) and (I_-) become

$$\begin{aligned} x \cot x \;&+\; (v^2 - x^2)^{\frac{1}{2}} \tanh[r(v^2 - x^2)^{\frac{1}{2}}] = 0 \;\; (I_+) \\ x \cot x \;&+\; (v^2 - x^2)^{\frac{1}{2}} \coth[r(v^2 - x^2)^{\frac{1}{2}}] = 0. \;\; (I_-) \end{aligned}$$

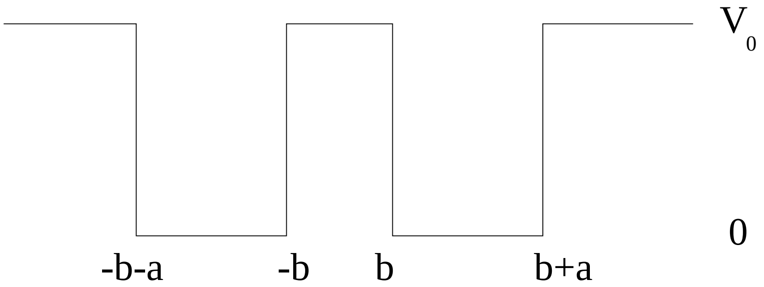
These can be solved for x, given r and v, using a maths package (e.g. *Mathematica's* "**Find Root**" command).

(a) Consider the case $v = 4, r = 1$. Find the two roots for x, one for I_+ and one for I_-, and the associated energy eigenvalues E_1^+ and E_1^- in units of V_0. [You will have to guess a starting value for x; for these parameters, $e^{-Kb} \ll 1$, so the equations both reduce to $-x \cot x = \sqrt{v^2 - x^2}$. Sketch the LHS and the RHS on the same plot, as functions of x, to estimate the root.] Explain the answers.

(b) Explore (i) smaller values of b; how do $E_1^\pm$ move? (ii) larger values of V_0; when do you get two more roots, $E_2^\pm$?

(c) Suppose $V_0 = 10$ eV, $a = 0.2$nm, $b = 0.1$ nm, and "m" is the electron mass. Find the two lowest energy eigenvalues in eV.

(v) The disk accompanying the book by Greenhow has a programme which solves a "finite double well" of the form



Compare the results for the 2 lowest levels with (iv)(c) above.

(vi) Let's return to the double well with infinite walls at $x = a+b, -a-b$. Sketch the wavefunctions for the ground (ψ_1^+) and first excited state (ψ_1^-), for a case like $v = 4$, $r = 1$ where these are the only bound states. Now suppose $\psi(x,t)$ is a solution of the time-dependent Schrödinger equation, such that

$$\psi(x, t = 0) = \psi_L(x) \equiv \frac{1}{\sqrt{2}}(\psi_1^+(x) + \psi_1^-(x))$$

Sketch $\psi_L(x, 0)$. Sketch also $\psi_R(x) = \frac{1}{\sqrt{2}}(\psi_1^+(x) - \psi_1^-(x))$. The time development of $\psi(x,t)$ is given by

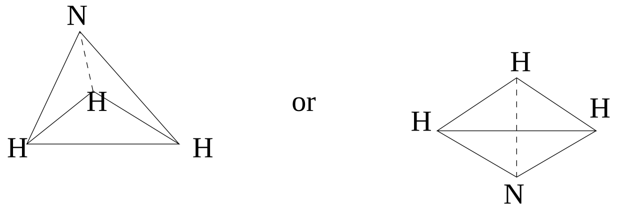
$$\psi(x,t) = \frac{1}{\sqrt{2}}\,(\psi_1^+(x)e^{-iE_1^+ t/\hbar} + \psi_1^-(x)e^{-iE_1^- t/\hbar}).$$

Show that this can be re-written as

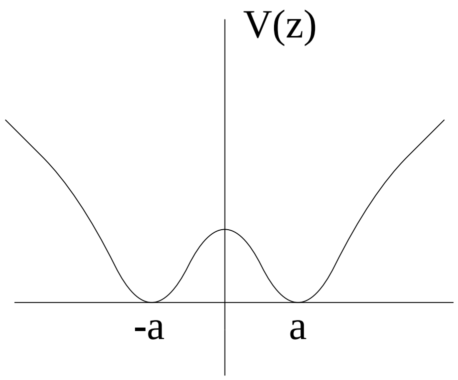
$$\psi(x,t) = e^{-i(E_1^+ + E_1^-)t/2\hbar}\left[\psi_L \cos\left(\frac{\omega t}{2}\right) + i\psi_R \sin\left(\frac{\omega t}{2}\right)\right]$$

where $\omega = (E_1^- - E_1^+)/\hbar$. Sketch $| \psi(x,t) |^2$ at $t = \frac{\pi}{2\omega}, \frac{\pi}{\omega}, \frac{3\pi}{2\omega}$ at $\frac{2\pi}{\omega}$. Clearly ω is the frequency of oscillation "$\psi_L \to \psi_R \to \psi_L$" for this wavefunction to oscillate between configurations mostly localised on one well, then on the other, and back again.

(vii) There are many applications of this kind of "quantum beats" phenomenon. A standard example is the ammonia molecule NH_3 (Feynman Vol III §8-6, chapter 9). We are interested in the position of the N relative to the plane of the three H's



There are two positions of equilibrium one "above" and one "below" the plane. Hence there must be two minima of the effective potential energy function, considered as a function of the coordinate z of the N, perpendicular to the H_3 plane (see picture below). For low-lying levels, this is something like our model double well. In this case, the splitting between the two lowest levels is $\sim\ 10^{-4}$eV. Calculate the "flip-flop" frequency ω (which is the frequency at which the ammonia maser operates), and the flip-flop period $2\pi/\omega$.



(viii) Returning to (I_+) and (I_-), for large values of Kb show that $\tanh Kb \approx 1 - 2e^{-2Kb}$ and that $\coth Kb \approx 1 + 2e^{-2Kb}$.

Show by a graphical method, as in (iv)(a), that the difference in energy $E_1^+ - E_1^-$ is of order $E_1 e^{-2Kb}$ where E_1 is the energy of the lowest state of a single well of the form

$$\begin{aligned} V(x) &= V_0 \ \text{ for } \ x < b \\ &= 0 \ \text{ for } \ b < x < a \\ &= \infty \ \text{ for } \ x \geq a. \end{aligned}$$

This shows that the flip-flop frequency depends exponentially on the width parameter b and the "height$-$energy" parameter $V_o - E$, characteristic of all "tunnelling" situations.

(ix) The periodic oscillations of $\mid \psi(x,t) \mid^2$ are a consequence of the delicate and precise *phase relationship* embodied in the superposition of $\psi_1^+(x)e^{-iE_1^+ t/\hbar}$ and $\psi_1^-(x)e^{iE_1^- t/\hbar}$. It is mathematically very similar to the coherent superposition which leads to the oscillating interference pattern in the "2-slit experiment". As in that case, if one inserts a relative phase between the two superposed amplitudes, and averages over it, the oscillations can be reduced or even removed ("decoherence"). Consider, for example, the superposition

$$\psi_\delta(x,t) = \frac{1}{\sqrt{2}} \left(\psi_1^+(x)e^{-iE_1^+ t/\hbar} + e^{i\delta}\psi_1^-(x)e^{-iE_1^- t/\hbar} \right)$$

Show that $\quad \mid \psi_\delta(x) \mid^2 = \psi_L(x)^2 \cos^2\left(\dfrac{\omega t - \delta}{2}\right) + \psi_R^2(x) \sin^2\left(\dfrac{\omega t - \delta}{2}\right).$

Suppose δ is randomly distributed over the interval $(-\pi, \pi)$. What is the average of $\mid \psi_\delta(x,t) \mid^2$? Suppose, instead, δ was distributed with a weight $\omega(\delta) = \frac{1}{2\pi}(1 + \cos\delta)$; what is the average of $\mid \psi_\delta(x,t) \mid^2$?

One way such a random phase can be introduced is by allowing the system to interact with some other object, which has many degrees of freedom, over which we have no control. "Measuring devices" are like that .... So some people have said that by taking such a quantum system described by such a superposition of amplitudes, in a double well, and measuring (repeatedly) its position one will introduce de-coherence and hence stop (or at any rate reduce) the oscillations

("Zeno's paradox", "a watched pot never boils"). See T.P. Altenmüller and A. Schengle, Physical Review A**49** (1994) 2016-2027. Not everyone agrees, however; see H. Fearn and W.E. Lamb, Physical Review A **46** (1992) 1199-1205. An analogous effect is claimed experimentally by A. Luis and J. Peřina, Physical Review Letters **76** (1996) 4340-43. The topic has been pursued in a recent M.Phys. project by David Wallace: see http://xxx.soton.ac.uk/abs/quant-ph/0004011.

<u>Angle - angular momentum uncertainty</u>

5. Consider a particle constrained to move on the circumference of a circle, so that the only dynamical variable is the azimuthal angle coordinate ϕ. The energy eigenvalues are given by the solution of

$$-\frac{\hbar^2}{2I}\,\frac{d^2\psi(\phi)}{d\phi^2} = E\psi(\phi)$$

where I is the "moment of inertia" (this is the quantum version of $L^2/2I$ where L is the angular momentum, $L = -i\hbar\frac{\partial}{\partial\phi}$).

(i) Show that if $\psi(\phi)$ is assumed to be single-valued, in the sense that $\psi(\phi = 0) = \psi(\phi = 2\pi)$, then the possible energy eigenvalues are $E_m = \frac{\hbar^2 m^2}{2I}$ with corresponding eigenfunctions $\psi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi}$ where m is an integer or zero, and where ψ_m has been normalised such that $\int_{-\pi}^{\pi} \mid \psi \mid^2 d\phi = 1$.

(ii) Suppose we want to make an amplitude which is quite well-defined in ϕ - for example,

$$\psi(\phi) = \frac{1}{\sqrt{\delta}}\; e^{iM\phi} \text{ for } -\frac{\delta}{2} \le \phi \le \frac{\delta}{2}, \text{ and } \psi = 0 \text{ for } \mid \phi \mid > \delta/2.$$

What is the average value of L_z for this ψ? This ψ is not an eigenfunction of L_z (why *not*?) but it can be expressed as a linear combination of L_z eigenfunctions via

$$\psi(\phi) = \sum_{m=-\infty}^{\infty} a_m \psi_m(\phi).$$

$$\text{Show that } a_m = \int_{-\pi}^{\pi} \psi_m^*(\phi)\psi(\phi)d\phi$$

and that this gives

$$a_m = \sqrt{\frac{\delta}{2\pi}} \frac{\sin[(M-m)\delta/2]}{[(M-m)\delta/2]}.$$

Sketch a_m versus m, assuming that $\delta \ll \pi$. Discuss the relation between δ ("the spread in ϕ") and the range of m values such that a_m is large ("the spread in $L_z/\hbar$").

(iii) for a particle in the state with amplitude $\psi(\phi)$, what is the probability that, if L_z was measured, the results would be (a) $M\hbar$? (b) $(M+1)\hbar$?

6. (i) Show that $[\phi, L_z] = i\hbar$. Taking the matrix element of this equation between states of the form $\psi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$, which are eigenfunctions of L_z, one finds

$$\langle \psi_{m_1} \mid \phi L_z - L_z \phi \mid \psi_{m_2} \rangle = i\hbar \int_0^{2\pi} \psi_{m_1}^* \psi_{m_2} d\phi.$$

Show that the RHS is $i\hbar\delta_{m_1 m_2}$. The first term on the LHS is $\hbar m_2 \langle \psi_{m_1} \mid \phi \mid \psi_{m_2} \rangle$, using $L_z \psi_{m_2} = \hbar m_2 \psi_{m_2}$.

In the second term we can use the Hermiticity of L_z to let it act to the left, on ψ_{m_1} (see Set 2 Q 8), so as to get $-\hbar m_1 \langle \psi_{m_1} \mid \phi \mid \psi_{m_2} \rangle$. So altogether we have

$$\hbar(m_2 - m_1)\langle \psi_{m_1} \mid \phi \mid \psi_{m_2} \rangle = i\hbar\delta_{m_1 m_2}.$$

But the right hand side is 1 if $m_1 = m_2$ while the LHS is 0. So $0 = 1$. Find the error in the argument.

(ii) Discuss what is wrong with concluding from

$$[\phi, L_z] = i\hbar$$

that

$$\Delta\phi \Delta L_z \geq \hbar/2,$$

even though from

$$[x, p] = i\hbar$$

one can properly conclude that

$$\Delta x \Delta p \geq \hbar/2.$$

7. <u>A slight case of non-linearity</u> (suitable for the vacation?)

Consider the following "alternative Schrödinger equation"

$$i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t} = \left\{-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}) - b\ \log[\mid \psi(\mathbf{r},t)\mid^2 a^3]\right\}\psi(\mathbf{r},t) \tag{1}$$

in which an additional piece has been added to the usual single-particle equation. This piece involves the log of $\mid \psi \mid^2$, and two new parameters a and b. "a" has dimension [length], so as to make the argument of the log dimensionless, since - see below - ψ will be normalisable in the usual way: $\int \mid \psi(\mathbf{r},t)\mid^2 d^3\mathbf{r} = 1$, and so $|\psi|^2$ has dimension $[\text{volume}]^{-1}$. b has dimension [energy].

(i) Show that if ψ and ϕ are separately solutions of this equation, then $\psi + \phi$ is *not* a solution, and more generally neither is any linear combination of ϕ and ψ. This is what is meant by saying that the equation is *non*-linear. Most wave equations you have met are linear, but that is almost invariably because some *approximation* has been made (look at the derivation of the equation for waves on a string, for instance). The wave equations of quantum mechanics are *postulated* to be linear, which is rather striking. Many people have wondered whether they might not actually also be approximations to some "truer" non-linear equations. We are going to look at the consequence of supposing the true non-linear equation to be (1).

(ii) Show that if $\rho = \mid \psi \mid^2$ and $j = \frac{\hbar}{2mi}(\psi^*\nabla\psi - (\nabla\psi^*)\psi)$ then the continuity equation

$$\frac{\partial\rho}{\partial t} + div\ j = 0$$

holds if ψ satisfies (1), so that we may retain the same forms for the probability density and probability current density as in the standard Schrödinger equation.

Can you extend the result to something more general than simply the log of $|\psi|^2$?

(iii) Show that if $\psi(\mathbf{r},t)$ is a solution of (1), then so is $\alpha\psi(\mathbf{r},t)\exp[(i/\hbar)\ bt\ \ell n \mid \alpha\mid^2]$ for arbitrary constant α. This implies that we may rescale ψ arbitrarily without loss of generality, choosing it to satisfy, for example, the standard normalisation condition $\int \mid \psi(\mathbf{r},t)\mid^2 d^3\mathbf{r} = 1$.

(iv) Consider the obvious generalisation of (1) to *two* particles. ψ becomes $\psi(\mathbf{r}_1, \mathbf{r}_2, t)$, $-\frac{\hbar^2}{2m}\nabla^2$ becomes $-\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2$ and U becomes $U(\mathbf{r}_1, \mathbf{r}_2)$. Suppose that $U(\mathbf{r}_1, \mathbf{r}_2) = V(\mathbf{r}_1) + V(\mathbf{r}_2)$. The absence of any term depending on both $\mathbf{r}_1$ and $\mathbf{r}_2$ means that the particles do not interact with each other, only with the potential U. In the standard theory, we should want $\psi(\mathbf{r}_1, \mathbf{r}_2, t) = \psi_1(\mathbf{r}_1, t)\psi_2(\mathbf{r}_2, t)$ for this situation, where ψ_1 and ψ_2 are solutions of the single particle equations with ∇_1^2 and V_1, ∇_2^2 and V_2, respectively. Show that this property is still true of (1). Why would it be a Bad Thing if it were not true? Give an example of a different non-linear term for which the "separability" property would not be true.

The results of (ii) - (iv) show that equation (1) is not such a bad equation to try. [It is discussed in *Annals of Physics 100* (1976) pages 62-937.]

(v) Consider the *one*-dimensional version with $U = 0$:

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = \left\{-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - b\ \log[\mid\psi\mid^2 a]\right\}\psi(x,t). \tag{2}$$

Verify that a normalised solution is

$$\psi(x,t) = (\ell\sqrt{\pi})^{-\frac{1}{2}}\exp(-x^2/2\ell^2).\exp(-iE_0t/\hbar)$$

if $\ell^2 = \hbar^2/2mb$. Interpreting E_0 as the energy eigenvalue, show that the effect of the constant "a" is merely to shift the energy scale, and that if it is chosen such that $\log(a/\ell\sqrt{\pi}) = 1$, the energy eigenvalue E_0 is zero for this solution.

Verify also that, with the same a,

$$\psi(x,t) = (\ell\sqrt{\pi})^{-\frac{1}{2}}\exp\left(-\frac{i}{\hbar}\,\frac{1}{2}mv^2t + \frac{i}{\hbar}mvx\right)\exp\left[-\frac{(x-vt)^2}{2\ell^2}\right]$$

is a solution of the full time-dependent equation (2). What is the physical appearance, and evolution in time, of $\mid\psi(x,t)\mid^2$? In particular, what is the physical interpretation of ℓ (and hence b)? Contrast this with a wave packet solution of the ordinary Schrödinger equation.

(vi) Consider equation (1) with $U = -e^2/4\pi\epsilon_0 r$, the Coulomb potential. Verify that a stationary state solution is

$$\psi(\mathbf{r}) = C\exp(-r^2/2\ell^2 - r/a_0)$$

where C is a constant determined from the normalisation (but you need not evaluate it) and a_0 is the Bohr radius; and check that this has energy eigenvalue

$$E = -E_0 + 3b - b\log(C^2 a^3)$$

where E_0 is the ground state energy in the standard theory.

(vii) On the basis of (vi), we can put on upper bound on the value of b, as follows. The Lamb shift measurements in hydrogen agree with theory at the level of about 0.1 Mc/s (see, for example, "Elementary Atomic Structure", Woodgate, pages 67-68).

Assuming, as in (vi), that the b term will produce a correction of order b, estimate an upper bound on b. For an even more restrictive bound, see an article by A. Shimony in Phys. Rev. A **70** (1979) p. 394, which proposes a neutron interferometer experiment. The result of the experiment is reported by C.G. Shull et al., Phys. Rev. Lett. **44** (1980) p. 765; they conclude $b < 3.4 \times 10^{-13} eV$.

8. <u>Covalent bonding in H_2^+ (see Feynman vol III chapter 10).</u>

Consider the system of two protons and one electron, *neglecting* the motion of the protons ($m_p \sim 2000\ m_e$). The Hamiltonian is

$$\begin{aligned} H &= -\frac{\hbar^2\nabla^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0 \mid \mathbf{r} - \mathbf{R}/2 \mid} - \frac{e^2}{4\pi\epsilon_0 \mid \mathbf{r} + \mathbf{R}/2 \mid} \\ &+ \left(\frac{e^2}{4\pi\epsilon_0 \mid \mathbf{R} \mid} = V_c, \text{a constant}\right) \end{aligned}$$

where $\mathbf{r}$ is the coordinate of the electron, $\mathbf{R}/2$ and $-\mathbf{R}/2$ are the (fixed) coordinates of the protons, and $\mathbf{R}$ is the inter-proton separation (the origin of coordinates in mid-way between the protons). As our two "basis states" we shall choose the lowest bound (hydrogenic) state of the electron centred on *each* proton; that is, one basis wave-function will be

$$u_1(\mathbf{r}, \mathbf{R}/2) \propto e^{-|\mathbf{r}-\mathbf{R}/2|/a_0}$$

(Coulomb wavefunction centred on $\mathbf{r} = \mathbf{R}/2$) and the other will be

$$u_2(\mathbf{r}, -\mathbf{R}/2) \propto e^{-|\mathbf{r}+\mathbf{R}/2|/a_0}.$$

Now these are not orthogonal, but if $\mathbf{R}$ is "reasonably large" the exponential tails will not overlap much and we can neglect $\int u_1^* u_2 d^3\mathbf{r}$.

So we shall approximate the exact energy eigenfunction by

$$\psi(\mathbf{r}) = au_1(\mathbf{r}, \mathbf{R}/2) + bu_2(\mathbf{r}, -\mathbf{R}/2)$$

for fixed $\mathbf{R}$. $\mid a \mid^2$ represents the probability that the electron will be found "on" the proton at $\mathbf{R}/2$, and similarly for $\mid b \mid^2$. The matrix elements of H are then as follows:-

(i)

$$H_{11} = \int u_1^* H u_1 d^3\mathbf{r} = E_0 + V_c - \int u_1^* \left(\frac{e^2}{4\pi\epsilon_0} \frac{1}{\mid \mathbf{r} + \mathbf{R}/2 \mid} \right) u_1 d^3\mathbf{r}$$

where E_0 is the energy of the hydrogenic ground state

(ii)

$$H_{22} = \int u_2^* H u_2 d^3\mathbf{r} = E_0 + V_c - \int u_2^* \left(\frac{e^2}{4\pi\epsilon_0} \frac{1}{\mid \mathbf{r} - \mathbf{R}/2 \mid} \right) u_2 d^3\mathbf{r}.$$

Show that in fact $H_{11} = H_{22} = \alpha$, say.

(iii) $H_{12} = \int u_1^* H u_2 d^3\mathbf{r}$: explain why (assuming $\int u_1^* u_2 d^3\mathbf{r} = 0$) $H_{12} = -\int u_1^* \frac{e^2}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{R}/2|} u_2 d^3\mathbf{r}$, and why $H_{21} = \int u_2^* H u_1 d^3\mathbf{r}$ is equal to H_{12}. Let this value be $-\beta (\beta > 0)$.

So the 2×2 matrix problem we are left with is

$$\begin{aligned} \alpha a \quad & -\beta b = Ea \\ -\beta a \quad & +\alpha b = Eb. \end{aligned}$$

Show that the eigenvalues are $E_- = \alpha - \beta$ for which $a = b$, and $E_+ = \alpha + \beta$ for which $a = -b$. So the wavefunction $\psi_- \sim au_1 + au_2$ has *lower* energy than either u_1 or u_2, and the $p + p + e^-$ system is *bound.* ψ_- is the "bonding orbital". Sketch ψ_- and ψ_+ as a function of $\mathbf{r}$ for fixed $\mathbf{R}$. Consider making $\mathbf{R}$ smaller, or bigger - how are $\psi_\pm$ affected? (If u_1 and u_2 are normalized, and approximately orthogonal, then $\psi_\pm$ are normalised if $a = \frac{1}{\sqrt{2}}$). Now consider

$$\beta \propto -\frac{e^2}{4\pi\epsilon_0}\int e^{-|\mathbf{r}-\mathbf{R}/2|/a_0}\frac{1}{\mid \mathbf{r}-\mathbf{R}/2 \mid}e^{-|\mathbf{r}+\mathbf{R}/2|/a_0}d^3\mathbf{r}.$$

Show that for large $\mid \mathbf{R} \mid$, $\beta \approx e^{-|\mathbf{R}|/a_0}$ times a function of $\mid \mathbf{R} \mid$ which is varying more slowly than an exponential.

So the difference in the energies of ψ_+ and ψ_- (which is 2β) gets larger as $\mid \mathbf{R} \mid$ decreases. However, as $\mid \mathbf{R} \mid$ gets smaller than about $2a$ (a = the Bohr radius in the hydrogen ground state), the $p - p$ repulsion V_c will begin to be important, and is positive, so eventually E_- will go positive for small $\mid \mathbf{R} \mid$. There will be a stable position at $\mid \mathbf{R} \mid \approx 2a$.

The energy of binding in the ψ_- state is β, which we can regard as an attractive "effective potential" acting between the two protons, due to "exchanging" the electron (remember, the wavefunction is a superposition of "on 1" and "on 2"). There is of course an energy price to be paid for removing one electron from one proton and putting it on the other - the price being about 13.6 eV. So there is an energy barrier for the electron to tunnel through. That is exactly why there is an exponential factor in β: if $\mid \mathbf{R} \mid$ gets much bigger than a, the tunnelling is very small.