Quantum Mechanics H.T. 2001

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Problem Set No. 6

Radial Schrödinger equation

1. The free particle stationary state Schrödinger equation in 3-D, separated in polar coordinates, leads to the radial equation

$$-\frac{\hbar^2}{2m}\,\frac{d^2X_\ell}{dr^2} + \frac{\ell(\ell+1)\hbar^2}{2mr^2}\,X_\ell = EX_\ell$$

where $\psi(r,\theta,\phi) = R_\ell(r)Y_{\ell m}(\theta,\phi) = \frac{1}{r}X_\ell(r)Y_{\ell m}(\theta,\phi)$. Verify that

$$\begin{aligned} X_0 &= A_0 \sin kr \\ X_1 &= A_1\left(\frac{\sin kr}{kr} - \cos kr\right) \end{aligned}$$

where A_0 and A_1 are constants, are solutions of the X_ℓ equation for $\ell = 0$ and $\ell = 1$ respectively.

[Harder: what is wrong with the solution $X_0 = B_0 \cos kr$ in the $l = 0$ case?]

The "spherical box" potential is defined by $V(r) = 0$ for $r \leq a$, $V(r) = \infty$ for $r > a$. This will force the boundary condition $R_\ell(r = a) = 0$. Give approximate numerical values, in units of $\frac{\hbar^2}{2ma^2}$, for the lowest *two* energy eigenvalues in each of the cases (a) $\ell = 0$ (b) $\ell = 1$. [$\ell = 0$ is easy; for $\ell = 1$ you need to solve the equation $\tan x = x$.]

2. The wavefunction $\phi(r)$ for a particle of mass m bound in a state with $\ell = 0$ in a 3-D radial well of depth V_0, and radius a (i.e. $V(r) = -V_0$ for $r \leq a$, $V(r) = 0$ for $r > a$) satisfies

$$-\frac{\hbar^2}{2m}\,\frac{1}{r^2}\,\frac{d}{dr}\,r^2\,\frac{d\phi}{dr} - V_0\phi = -E\phi \text{ for } r \leq a$$

$$-\frac{\hbar^2}{2m}\,\frac{1}{r^2}\,\frac{d}{dr}\,r^2\,\frac{d\phi}{dr} = -E\phi \text{ for } r > a$$

where E is the binding energy (> 0). Check that the solution has the form $\phi = \frac{A}{r}\sin kr$ for $r \leq a$, $\phi = \frac{B}{r}e^{-Kr}$ for $r > a$, where $\frac{\hbar^2 k^2}{2m} = (V_0 - E)$ and $\frac{\hbar^2 K^2}{2m} = E$, and where A and B are constants. Deduce from the boundary conditions at $r = a$

that energy eigenvalues are obtained from the equation $k \cot ka = -K$. Show (refer back to Set 4 Q 1) that there is no allowed E value if $V_0 < \hbar^2\pi^2/8ma^2$. Evaluate this critical value of V_0 (needed to bind a particle) in MeV, for $m = \frac{1}{2}$ mass of proton, and $a = 2 \times 10^{-15}$m (these are roughly the parameters for the deuteron, the neutron-proton bound state which forms the nucleus of deuterium). Why is $\frac{1}{2}$ the proton mass taken? (If in doubt, see Q 6 below.)

3. (i) What quantum numbers are needed to describe the state of an electron (neglecting spin) in hydrogen? Why is it possible to obtain states with simultaneously well defined eigenvalues of $\hat{H}$, $\hat{\mathbf{L}}^2$ and of $\hat{L}_z$?

   (ii) From Set 2 Q 9 (iii) we know that the ground state wavefunction in hydrogen is proportional to $e^{-r/a}$, where $a = 4\pi\epsilon_0\hbar^2/me^2$. Normalise this wavefunction (N.B. get the volume element right!).

   (iii) $\mid \psi(x,y,z) \mid^2 dxdydz$ is the probability for finding a particle between (x,y,z) and $(x+dx, y+dy, z+dz)$. In r, θ, ϕ this becomes $\mid \psi(r,\theta,\phi) \mid^2 r^2 \sin\theta d\theta d\phi dr$. So the probability of finding the particle between r and $r+dr$, without caring about its angular position, is $[\int\int \mid \psi(r,\theta,\phi) \mid^2 \sin\theta d\theta d\phi] r^2 dr$.

   Writing $\psi = R_{n\ell}(r) Y_{\ell m}(\theta,\phi)$ show that this probability is just $\mid R_{n\ell}(r) \mid^2 r^2 dr$, so that the radial probability density is $r^2 \mid R_{n\ell}(r) \mid^2$. Sketch this density for the ground state wavefunction. Find the value of r for which it is a maximum. Also calculate the average value of r in this state.

   [Extra: The programme "Schrödinger equation: central potentials Coulomb potential" in McMurry's disk can be run to show the Coulomb wavefunctions for various n and ℓ. Verify (a) that for each state with definite n and ℓ, there are $n-\ell-1$ nodes in $r^2 R_{n\ell}^2$ (in addition to the "automatic" zero at the origin) (b) that $r^2 R_{n\ell}^2$ has $n-\ell$ maxima, increasing in height with distance from the origin.]

4. (i) Consider the two-dimensional SHO of Q 5 Set 4. Show that the eigenvalue of $\hat{L}_z$ is a good quantum number. What is the $\hat{L}_z$ eigenvalue of the ground state?

   The two (degenerate) wavefunctions for the first excited state found in Q 5 Set 4 had the form

$$\begin{aligned} \psi_{10} &\propto xe^{-x^2/2a^2} e^{-y^2/2a^2} \\ \psi_{01} &\propto ye^{-x^2/2a^2} e^{-y^2/2a^2} \end{aligned}$$

   Are these eigenfunctions of $\hat{L}_z$? Show that linear combinations of these wavefunctions can be found which are $\hat{L}_z$ eigenfunctions, and state the $\hat{L}_z$ eigenvalues.

   (ii) Consider a particle moving in 3-D subject to a potential $V = \frac{1}{2}m\omega^2(x^2+y^2+z^2)$. Writing $\psi(x,y,z) = X(x)Y(y)Z(z)$ show that the time-independent Schrödinger equation can be solved in terms of the solutions for the 1-D oscillator. Assuming the 1-D results, show that the energy eigenvalues are

$$E(n_x, n_y, n_z) = \hbar\omega(\frac{3}{2} + n_x + n_y + n_z)$$

where the n's are integers ≥ 0. What is the degeneracy of the levels with (a) $E = 3\hbar\omega/2$, (b) $E = 5\hbar\omega/2$, and (c) $E = 7\hbar\omega/2$? Are the eigenvalues of $\hat{\mathbf{L}}^2$ and $\hat{L}_z$ good quantum numbers for this Hamiltonian?

Try to guess the values of ℓ associated with the above three energy eigenvalues (remember that there are $2\ell+1$ states with the same ℓ, and different m, which will be degenerate, here).

Write down the (un-normalised) wavefunctions for all the states with $E = \frac{3}{2}\hbar\omega$ and $E = \frac{5}{2}\hbar\omega$, and verify the values you guessed for ℓ (using known facts about the $Y_{\ell m}$'s). Show how linear combinations of your eigenfunctions with $E = \frac{5}{2}\hbar\omega$ can be chosen to have definite $\hat{L}_z$ values; what are these $\hat{L}_z$ values?

Finally, compare the energy spectrum and degeneracies for the Coulomb problem and the 3-D oscillator problem.

Schrödinger equation for two particles

5. *Independent motion.* Write down, but do not try to solve, the time-independent Schrödinger equation for the Helium atom (assuming the nucleus is infinitely heavy). Now suppose you neglect the potential which acts between the electrons. Solve the resulting approximate equation by an appropriate "separation of variables" i.e. write $\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)$ where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the coordinates of the electrons. Identify the separate equations for $\psi_1(\mathbf{r}_1)$ and $\psi_2(\mathbf{r}_2)$ as hydrogen - like Schrödinger equations with e^2 replaced by $2e^2$. Hence calculate the energy of the ground state of the He atom in this approximation, relative to the ground state of the He^{++} ion. The real value is -79 eV. What is the major cause of the discrepancy? Estimate roughly the magnitude of the correction you have proposed.

6. *Relative and centre-of-mass separation.* (i) Consider two particles with masses m_1 and m_2, in 1-D, with the potential energy $V(x_1 - x_2)$. The stationary state Schrödinger equation is

$$\left[-\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial x_2^2} + V(x_1 - x_2)\right]\Psi(x_1, x_2) = E\Psi(x_1, x_2).$$

Why can this equation *not* be separated in the coordinates x_1 and x_2 ?

(ii) Define the centre of mass coordinate $X = (m_1 x_1 + m_2 x_2)/M$ where $M = m_1 + m_2$, and the relative coordinate

$$x = x_1 - x_2.$$

By using the chain rule in the form

$$\frac{\partial f}{\partial x_1} = \frac{\partial f}{\partial X}\frac{\partial X}{\partial x_1} + \frac{\partial f}{\partial x}\frac{\partial x}{\partial x_1}$$

(or, better, in the operator form

$$\frac{\partial}{\partial x_1} = \frac{\partial X}{\partial x_1}\frac{\partial}{\partial X} + \frac{\partial x}{\partial x_1}\frac{\partial}{\partial x},$$

and similarly for $\frac{\partial}{\partial x_2}$) show that the Schrödinger equation can be re-written as

$$\left[-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial X^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + V(x)\right]\Psi(x, X) = E\Psi$$

where the *reduced mass* μ is equal to $m_1 m_2/(m_1 + m_2)$.

(iii) Show that this equation can be separated in the coordinates x and X i.e. solutions can be found of the form

$$\Psi(x, X) = \psi_{rel}(x)\psi_{CM}(X).$$

Obtain the equation satisfied by $\psi_{rel}(x)$.

(iv) What is the solution of the equation for $\psi_{CM}(X)$? Explain the answer physically.

The addition of angular momenta

Note: this topic is outside the Part A QM syllabus, but it will certainly be useful for Atomic, Nuclear and Particle physics in due course.

7. Here we are considering a system of two non-interacting particles with angular momentum operators $\hat{\boldsymbol{L}}^{(1)}$ and $\hat{\boldsymbol{L}}^{(2)}$ respectively; the total angular momentum operator is $\hat{\boldsymbol{L}} = \hat{\boldsymbol{L}}^{(1)} + \hat{\boldsymbol{L}}^{(2)}$. We denote the eigenvalues of $\hat{\boldsymbol{L}}^{(1)}.\hat{\boldsymbol{L}}^{(1)}$ and $\hat{L}_z^{(1)}$ by $\ell_1(\ell_1 + 1)\hbar^2$ and $m_1\hbar$ respectively (and similarly for particle 2). We denote the eigenvalues of $\hat{\boldsymbol{L}}.\hat{\boldsymbol{L}}$ and $\hat{L}_z$ by $L(L+1)\hbar^2$ and $M\hbar$ respectively.

(a) Consider the angular momenta of two particles which are each in $\ell = 1$ states. How many states of the form $\phi_{\ell_1=1,m_1}(\boldsymbol{r}_1)\phi_{\ell_2=1,m_2}(\boldsymbol{r}_2)$ have $\hat{L}_z$ quantum number $M = 2$? Repeat the exercise for $M = 1, 0, -1, -2$ and comment on any symmetry in the results; how many states do you get altogether? According to the triangle rule the total angular momentum quantum number could be $L = 2, 1$, or 0; how many of these states are there altogether? Now make sure you have the same number of states in the (L, M) labelling as in the $(\ell_1, m_1, \ell_2, m_2)$ labelling.

(b) How many states of the form $\phi_{\ell_1,m_1}(\boldsymbol{r}_1)\phi_{\ell_2,m_2}(\boldsymbol{r}_2)$ have $\hat{L}_z$ quantum number $M = \ell_1 + \ell_2$? How many have $\hat{L}_z$ quantum number $M = \ell_1 + \ell_2 - 1$? Carry on until you get to "How many have $\hat{L}_z$ quantum number $M = 0$?" – why is it not necessary to go any further? Now explain how these results are consistent with the possible L values being $\ell_1 + \ell_2, \ell_1 + \ell_2 - 1, \ldots, |\ell_1 - \ell_2|$ which is what the triangle rule of addition tells us. Why can we not have $L > \ell_1 + \ell_2$?

(c) As discussed briefly in the lectures there are in fact states with half-integer angular momentum quantum numbers. For example the electron and proton both have a half-integer intrinsic spin (usually denoted $\boldsymbol{s}$). This means that the wavefunction satisfies $\boldsymbol{s}^2\psi = \hbar^2 s(s+1)\psi$ and $s_z\psi = \hbar m_s\psi$ with $s = 1/2$ and $m_s = +1/2$ or $m_s = -1/2$. All pairs of angular momenta, whether integer or half-integer, combine according to exactly the same rules as pairs of orbital angular momenta.

The ground state of hydrogen has no orbital angular momentum so its total angular momentum, quantum number I, comes entirely from the electron and proton spins. What are the possible values of I? Now consider an $\ell = 1$ state of the hydrogen atom; what are the possible values of I now?