Homework No. 09 (Spring 2015)

PHYS 530A: Quantum Mechanics II

Due date: Tuesday, 2015 May 5, 4.30pm

1. The Hamiltonian for an hydrogenic atom is

$$H = \frac{p^2}{2\mu} - \frac{Ze^2}{r}. \tag{1}$$

(a) Using

$$\mathbf{p} = \frac{\hbar}{i}\boldsymbol{\nabla} \qquad \text{and} \qquad H = -\frac{\hbar}{i}\frac{\partial}{\partial t} \tag{2}$$

in conjunction with the fact that Hamiltonian is a constant of motion, construct the 'time-independent Schrödinger equation' for hydrogenic wavefuntions to be

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{r}\right)\psi_n(\mathbf{r}) = E_n\psi_n(\mathbf{r}). \tag{3}$$

(b) We shall confine our discussion to bound states ($E_n < 0$). Define

$$E_n = -\frac{\mu Z^2 e^4}{2\hbar^2}\frac{1}{n^2} \qquad \text{and} \qquad a_0 = \frac{\hbar^2}{\mu e^2}, \tag{4}$$

later being the (first) Bohr radius. Thus, derive

$$\left(\nabla^2 + \frac{2Z}{a_0 r}\right)\psi_n(\mathbf{r}) = \frac{Z^2}{a_0^2}\frac{1}{n^2}\psi_n(\mathbf{r}). \tag{5}$$

(c) The Laplacian in spherical polar coordinates is

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right). \tag{6}$$

Since angular momentum is a constant of motion we can expand the wavefunctions in the form

$$\psi_n(\mathbf{r}) = \sum_{l=0}^{n-1}\sum_{m=-l}^{l} R_{nl}(r)Y_{lm}(\theta,\phi), \tag{7}$$

where the spherical harmonics satisfy

$$L^2 Y_{lm}(\theta,\phi) = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) = \hbar^2 l(l+1)Y_{lm}(\theta,\phi). \tag{8}$$

Thus, derive the differential equation for the radial part of the wavefunction as

$$\left[\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} - \frac{l(l+1)}{r^2} + \frac{2Z}{a_0 r} - \frac{Z^2}{a_0^2 n^2}\right]R_{nl}(r) = 0. \tag{9}$$

(d) In terms of the dimensionless variable

$$x = \frac{2Zr}{a_0} \tag{10}$$

derive

$$\left[\frac{d^2}{dx^2} + \frac{2}{x}\frac{d}{dx} - \frac{l(l+1)}{x^2} + \frac{1}{x} - \frac{1}{(2n)^2} \right] R_{nl}(x) = 0. \tag{11}$$

(e) For $x \gg 1$ argue that we have

$$\left[\frac{d^2}{dx^2} - \frac{1}{(2n)^2} \right] R_{nl}(x) = 0. \tag{12}$$

Solve this equation to learn the asymptotic behaviour of the radial wavefunction to be

$$R_{nl}(x) \sim e^{-\frac{x}{2n}} \qquad \text{for} \qquad x \gg 1. \tag{13}$$

(f) For $x \ll 1$ argue that we have

$$\left[\frac{1}{x^2}\frac{d}{dx}x^2\frac{d}{dx} - \frac{l(l+1)}{x^2} \right] R_{nl}(x) = 0. \tag{14}$$

Solve this equation to learn the limiting behaviour of the radial wavefunction to be

$$R_{nl}(x) \sim x^l \qquad \text{for} \qquad x \ll 1. \tag{15}$$

(g) Use the above limiting forms to define

$$R_{nl}(x) = x^l e^{-\frac{x}{2n}} L(x), \tag{16}$$

and derive, in terms of

$$y = \frac{x}{n}, \tag{17}$$

$$\left[y\frac{d^2}{dy^2} + \{(2l+1) + 1 - y\}\frac{d}{dy} + (n - l - 1) \right] L(y) = 0. \tag{18}$$

Compare this to the differential equation satisfied by the Laguerre polynomials, $L_n^{(\alpha)}(y)$, the Laguerre equation,

$$\left[y\frac{d^2}{dy^2} + \{\alpha + 1 - y\}\frac{d}{dy} + n \right] L_n^{(\alpha)}(y) = 0. \tag{19}$$

Thus, derive

$$R_{nl}(r) = N \left(\frac{2Zr}{na_0} \right)^l e^{-\frac{Zr}{na_0}} L_{n-l-1}^{(2l+1)} \left(\frac{2Zr}{na_0} \right), \tag{20}$$

where N is a normalization constant.

(h) The normalization constant N is, in principle, determined using

$$\int_0^\infty r^2 dr |R_{nl}(r)|^2 = 1. \tag{21}$$

Verify that, the above statement does not, immediately, lead to the orthogonality relation for Laguerre polynomials,

$$\int_0^\infty dx\, x^\alpha e^{-x} L_n^{(\alpha)}(x) L_{n'}^{(\alpha)}(x) = \delta_{nn'} \frac{(n+\alpha)!}{n!}. \tag{22}$$

(i) Let us derive the Hellmann-Feynman theorem. Consider the energy eigenvalue equation

$$[H(\lambda) - E(\lambda)]|E, \lambda\rangle = 0 \tag{23}$$

and its adjoint

$$\langle E, \lambda|[H(\lambda) - E(\lambda)] = 0. \tag{24}$$

Differentiate with respect to λ:

$$\left(\frac{\partial E}{\partial \lambda} - \frac{\partial H}{\partial \lambda}\right)|E, \lambda\rangle + (E - H)|E, \lambda\rangle = 0, \tag{25}$$

and multiply with $\langle E, \lambda|$ to obtain

$$\left\langle \frac{\partial H}{\partial \lambda} \right\rangle = \langle E, \lambda| \frac{\partial H}{\partial \lambda} |E, \lambda\rangle = \frac{\partial E}{\partial \lambda}, \tag{26}$$

which is the statement of the Hellmann-Feynman theorem.

(j) Use the Hellmann-Feynman theorem, by regarding λ as Z, in the hydrogenic atom to evaluate

$$\left\langle \frac{1}{r} \right\rangle_n = \int_0^\infty r^2 dr\, \frac{1}{r}\, |R_{nl}(r)|^2 = \frac{Z}{a_0 n^2}. \tag{27}$$

(k) Use the orthogonality relation of Laguerre polynomials in Eq. (22) in Eq. (27) to derive the normalization constant N as

$$N = \frac{2}{n^2} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \sqrt{\frac{(n-l-1)!}{(n+l)!}}. \tag{28}$$

Thus, derive the hydrogenic wavefunction

$$\psi_{nlm}(\mathbf{r}) = \frac{2}{n^2} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \sqrt{\frac{(n-l-1)!}{(n+l)!}} \left(\frac{2Zr}{na_0}\right)^l e^{-\frac{Zr}{na_0}} L_{n-l-1}^{(2l+1)} \left(\frac{2Zr}{na_0}\right) Y_{lm}(\theta, \phi). \tag{29}$$

2. In this problem we shall construct the eigenfunction $\psi_{n,n-1,n-1}(\mathbf{r})$.

(a) Since $|n, n-1, n-1\rangle$ is in the highest possible l and m, we have

$$J_+^{(1)}|n, n-1, n-1\rangle = 0 \qquad \text{and} \qquad J_+^{(2)}|n, n-1, n-1\rangle = 0. \tag{30}$$

Thus, conclude that

$$L_+|n, n-1, n-1\rangle = 0 \qquad \text{and} \qquad \hbar n\, A_+|n, n-1, n-1\rangle = 0. \tag{31}$$

(b) Show that

$$Y_{n-1,n-1}(\theta, \phi) \sim \left(\frac{x+iy}{r}\right)^{n-1}. \tag{32}$$

Thus, construct the eigenfunction to have the form

$$\psi_{n,n-1,n-1}(r, \theta, \phi) = (x+iy)^{n-1} f_n(r). \tag{33}$$

(c) Show that

$$f_n(r) = Ce^{-\frac{Zr}{na_0}}, \tag{34}$$

where C is a normalization constant. Thus, derive

$$\psi_{n,n-1,n-1}(r, \theta, \phi) = C(r \sin\theta e^{i\phi})^{n-1} e^{-\frac{Zr}{na_0}}. \tag{35}$$

(d) Requiring

$$\int d^3r |\psi_{n,n-1,n-1}(r, \theta, \phi)|^2 = 1, \tag{36}$$

which involves the integral

$$I_l = \frac{1}{2}\int_{-1}^{1} dt(1-t^2)^l, \tag{37}$$

determine the normalization constant (upto a phase) to be

$$|C| = \frac{2}{n^2}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(\frac{2Z}{na_0}\right)^{n-1}\frac{1}{\sqrt{4\pi}}\frac{1}{2^{n-1}(n-1)!}. \tag{38}$$

Hint: Evaluate I_l using integration by parts to notice

$$I_l = \frac{2l}{2l+1} I_{l-1}, \tag{39}$$

and iterate this relation to yield

$$I_l = \frac{(2^l l!)^2}{(2l+1)!}. \tag{40}$$

(e) Verify that the solution is indeed

$$\psi_{n,n-1,n-1}(r, \theta, \phi) = R_{n,n-1}(r) Y_{n-1,n-1}(\theta, \phi). \tag{41}$$