Final Exam (Spring 2018)

PHYS 530A: Quantum Mechanics II

Date: 2018 May 8

1. (**110 points.**) The Hamiltonian for an hydrogenic atom is

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

   (a) The eigenvalue equation for the hydrogenic atom is

$$H|E_n\rangle = E_n|E_n\rangle, \tag{2}$$

   where $H' = E_n$ are the eigenvalues of the Hamiltonian H. Projecting the above eigenvalue equation on to the position basis we obtain

$$\langle \mathbf{r}|H|E_n\rangle = E_n\langle \mathbf{r}|E_n\rangle. \tag{3}$$

   The projection of the energy eigenfunctions $|E_n\rangle$ on to the position basis

$$\psi_n(\mathbf{r}) = \langle \mathbf{r}|E_n\rangle. \tag{4}$$

   are defined as the hydrogenic wavefunctions. Starting from Eq. (3) show that the hydrogenic wavefunction satisfies the 'time-independent Schrödinger equation'

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{r}\right)\psi_n(\mathbf{r}) = E_n\psi_n(\mathbf{r}). \tag{5}$$

   The effectively involves the substitution

$$\mathbf{p} = \frac{\hbar}{i}\boldsymbol{\nabla} \tag{6}$$

   in the Hamiltonian.

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

$$E_n = -\frac{\mu Z^2 e^4}{2\hbar^2}\frac{1}{n^2} \qquad \text{and} \qquad a_0 = \frac{\hbar^2}{\mu e^2}, \tag{7}$$

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

$$\left(\nabla^2 + \frac{2Z}{a_0 r}\right)\psi_n(\mathbf{r}) = \frac{Z^2}{a_0^2}\frac{1}{n^2}\psi_n(\mathbf{r}). \tag{8}$$

(c) The Laplacian in spherical polar coordinates is

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right). \tag{9}$$

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

$$\psi_n(\mathbf{r}) = \sum_{l=0}^{n-1}\sum_{m=-l}^{l} R_{nl}(r)Y_{lm}(\theta,\phi), \tag{10}$$

where the spherical harmonics satisfy

$$L^2 Y_{lm}(\theta,\phi) = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) = \hbar^2 l(l+1)Y_{lm}(\theta,\phi). \tag{11}$$

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

$$\left[\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} - \frac{l(l+1)}{r^2} + \frac{2Z}{a_0 r} - \frac{Z^2}{a_0^2 n^2}\right]R_{nl}(r) = 0. \tag{12}$$

(d) In terms of the dimensionless variable

$$x = \frac{2Zr}{a_0} \tag{13}$$

derive

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

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

$$\left[\frac{d^2}{dx^2} - \frac{1}{(2n)^2}\right]R_{nl}(x) = 0. \tag{15}$$

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

$$R_{nl}(x) \sim e^{-\frac{x}{2n}} \qquad \text{for} \qquad x \gg 1. \tag{16}$$

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

$$\left[\frac{1}{x^2}\frac{d}{dx}x^2\frac{d}{dx} - \frac{l(l+1)}{x^2}\right]R_{nl}(x) = 0. \tag{17}$$

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

$$R_{nl}(x) \sim x^l \qquad \text{for} \qquad x \ll 1. \tag{18}$$

(g) Use the above limiting forms to define

$$R_{nl}(x) = x^l e^{-\frac{x}{2n}} L(x), \tag{19}$$

and derive, in terms of

$$y = \frac{x}{n}, \tag{20}$$

$$\left[y \frac{d^2}{dy^2} + \{(2l+1) + 1 - y\} \frac{d}{dy} + (n - l - 1) \right] L(y) = 0. \tag{21}$$

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

$$\left[y \frac{d^2}{dy^2} + \{\alpha + 1 - y\} \frac{d}{dy} + n \right] L_n^{(\alpha)}(y) = 0. \tag{22}$$

Thus, derive

$$R_{nl}(r) = N \left(\frac{2Zr}{na_0} \right)^l e^{-\frac{Zr}{na_0}} L_{n-l-1}^{(2l+1)} \left(\frac{2Zr}{na_0} \right), \tag{23}$$

where N is a normalization constant.

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

$$\int_0^\infty r^2 dr |R_{nl}(r)|^2 = 1. \tag{24}$$

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

$$\int_0^\infty dx\, x^\alpha e^{-x} L_n^{(\alpha)}(x) L_{n'}^{(\alpha)}(x) = \delta_{nn'} \frac{(n+\alpha)!}{n!}. \tag{25}$$

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

$$[H(\lambda) - E(\lambda)] |E, \lambda\rangle = 0 \tag{26}$$

and its adjoint

$$\langle E, \lambda | [H(\lambda) - E(\lambda)] = 0. \tag{27}$$

Differentiate with respect to λ:

$$\left(\frac{\partial E}{\partial \lambda} - \frac{\partial H}{\partial \lambda} \right) |E, \lambda\rangle + (E - H) |E, \lambda\rangle = 0, \tag{28}$$

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

$$\left\langle \frac{\partial H}{\partial \lambda} \right\rangle = \langle E, \lambda | \frac{\partial H}{\partial \lambda} | E, \lambda\rangle = \frac{\partial E}{\partial \lambda}, \tag{29}$$

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

$$\left\langle \frac{1}{r} \right\rangle_n = \int_0^\infty r^2 dr \, \frac{1}{r} \, |R_{nl}(r)|^2 = \frac{Z}{a_0 n^2}. \tag{30}$$

(k) Use the orthogonality relation of Laguerre polynomials in Eq. (25) in Eq. (30) to derive the normalization constant N as

$$N = \frac{2}{n^2} \left(\frac{Z}{a_0} \right)^{\frac{3}{2}} \sqrt{\frac{(n-l-1)!}{(n+l)!}}. \tag{31}$$

Thus, derive the radial part of the hydrogenic wavefunction

$$R_{nl}(r) = \frac{2}{n^2} \left(\frac{Z}{a_0} \right)^{\frac{3}{2}} \sqrt{\frac{(n-l-1)!}{(n+l)!}} \left(\frac{2Zr}{na_0} \right)^l e^{-\frac{Zr}{na_0}} L_{n-l-1}^{(2l+1)} \left(\frac{2Zr}{na_0} \right). \tag{32}$$