

Phys 522: Problem Set 6

Solutions

Problem 1: Dipole matrix elements

$$\hat{H}_{int} = -\hat{d} \cdot \vec{E}, \quad \hat{d} = -e\hat{x} \quad (\text{Electric dipole operator})$$

(a) Matrix elements between two energy eigenstates of the Hydrogen atom:

$$\langle n', l', m' | \hat{H}_{int} | n, l, m \rangle$$

Now recall the unitary "parity" transformation

$$\hat{\Pi}^\dagger \hat{x} \hat{\Pi} = -\hat{x} \quad \Rightarrow \quad \hat{\Pi}^\dagger \hat{H}_{int} \hat{\Pi} = -\hat{H}_{int} \quad (\text{odd under parity})$$

Parity conservation $\Rightarrow \hat{\Pi}$ unitary

$$\hat{\Pi}^\dagger \hat{\Pi} = \hat{1}$$

$$\begin{aligned} \Rightarrow \langle n', l', m' | \hat{H}_{int} | n, l, m \rangle &= \langle n', l', m' | \hat{\Pi}^\dagger \hat{\Pi} \hat{H}_{int} \hat{\Pi}^\dagger \hat{\Pi} | n, l, m \rangle \\ &= -\langle n', l', m' | \hat{\Pi}^\dagger \hat{H}_{int} \hat{\Pi} | n, l, m \rangle \end{aligned}$$

Aside: $\hat{\Pi} | n, l, m \rangle = | n, l \rangle \otimes \hat{\Pi} | l, m \rangle$

(The parity operation leaves the radial wave function unchanged since this only depends on $r^2 = |\vec{x}|^2$)

However recall that the $Y_{l,m}$'s are eigenfunctions of parity with eigenvalue $(-1)^l$

$$\Rightarrow \hat{\Pi} | n, l, m \rangle = (-1)^l | n, l, m \rangle$$

$$\Rightarrow \langle n', l', m' | \hat{H}_{int} | n, l, m \rangle = -(-1)^{l+l'} \langle n', l', m' | \hat{H}_{int} | n, l, m \rangle$$

\Rightarrow Matrix element vanishes unless $(-1)^{l+l'} = -1$ $| n', l', m' \rangle$ and $| n, l, m \rangle$ must have opposite parity

(b) We write the interaction Hamiltonian in the form $\hat{H}_{int} = e \mathcal{E}_i \hat{x}_i$

where $x_1 = x$, $x_2 = y$, $x_3 = z$

The matrix element of interest is:

$$\langle \underbrace{21m'}_{2p_m} | \hat{H}_{int} | \underbrace{100}_{1s_0} \rangle = e \mathcal{E}_i \langle 21m' | \hat{x}_i | 100 \rangle$$

$$= \int d^3x R_{21}(r) Y_{1m'}^*(\theta, \phi) \hat{x}_i R_{10}(r) Y_{00}(\theta, \phi)$$

To do these integrals, we express x, y, z in spherical coordinates, and then in spherical harmonics.

Aside:

$$x = r \sin \theta \cos \phi, \quad y = r \sin \theta \sin \phi, \quad z = r \cos \theta$$

$$Y_{0,0}(\theta, \phi) = \frac{1}{\sqrt{4\pi}}$$

$$Y_{1,0}(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos \theta = \sqrt{\frac{3}{4\pi}} \frac{z}{r}$$

$$Y_{1,\pm 1}(\theta, \phi) = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\mp i\phi} = \mp \sqrt{\frac{3}{8\pi}} \left(\frac{x \pm iy}{r} \right)$$

$$\Rightarrow x = \sqrt{\frac{2\pi}{3}} r (-Y_{1,1}(\theta, \phi) + Y_{1,-1}(\theta, \phi))$$

$$y = \sqrt{\frac{2\pi}{3}} r (+i Y_{1,1}(\theta, \phi) + Y_{1,-1}(\theta, \phi))$$

$$z = \sqrt{\frac{4\pi}{3}} r Y_{1,0}(\theta, \phi)$$

◦ Consider first $\hat{E}^{(1)}$ along z

$$\langle 2p_m | \hat{H}_{int} | 1s_0 \rangle = e E \sqrt{\frac{4\pi}{3}} \int_0^\infty dr r^3 R_{21}(r) R_{10}(r)$$

$$\int d\Omega Y_{1,m}^* Y_{1,0} Y_{00} \leftarrow \sqrt{\frac{4}{\pi}}$$

= δ_{m0} by orthonormality of $Y_{l,m}$'s

$$\Rightarrow = \frac{e E r_0}{\sqrt{3}} \int dr r^3 R_{21}(r) R_{10}(r) \delta_{m,0}$$

Aside: $\int_0^\infty dr r^3 R_{21}(r) R_{10}(r) = a_0 \int_0^\infty d\bar{r} \bar{r} u_{21}(\bar{r}) u_{10}(\bar{r})$

where $u_{nl}(r) = r R_{nl}(r)$ (reduced radial wave function)
and $\bar{r} \equiv \frac{r}{a_0}$

For Hydrogen $u_{nl}(\bar{r}) = \underbrace{C_{nl}}_{\text{Normalization}} \bar{r}^{l+1} e^{-\frac{\bar{r}}{n}} \underbrace{L_{n-l-1}^{2l+1}\left(\frac{2\bar{r}}{n}\right)}_{\text{Laguerre polynomial}}$

$$\Rightarrow \int_0^\infty d\bar{r} \bar{r} u_{21}(\bar{r}) u_{10}(\bar{r}) = \frac{1}{\sqrt{6}} \int_0^\infty d\bar{r} \bar{r}^4 e^{-\frac{3}{2}\bar{r}} \approx 1.3$$

\Rightarrow For $\hat{E}^{(1)}$ along z ,

$$\langle 2p, m=0 | e E \hat{z} | 1s, m=0 \rangle = (e a_0 E) \frac{1.3}{\sqrt{3}} \approx 0.75 e a_0 E$$

(c) We consider now circularly rotating electric fields:

$$\vec{E}(t) = \text{Re} [E_0 (\vec{e}_x \pm i\vec{e}_y) e^{-i\omega t}] = \mp \sqrt{2} \text{Re} [E_0 \vec{e}_{\pm} e^{-i\omega t}], \text{ where } \vec{e}_{\pm} = \mp \left(\frac{\vec{e}_x \pm i\vec{e}_y}{\sqrt{2}} \right)$$

The matrix element of interest is now

$$\langle n' l' m' | \hat{x} \cdot \vec{e}_{\pm} | n l m \rangle = \langle n' l' m' | \mp \left(\frac{\hat{x} \pm i\hat{y}}{\sqrt{2}} \right) | n l m \rangle$$

$$\text{Recall } r Y_{l, \pm 1}(\theta) = \mp \sqrt{\frac{3}{8\pi}} r \sin\theta e^{\pm i\phi} = \mp \sqrt{\frac{3}{4\pi}} \left(\frac{x \pm iy}{r} \right)$$

$$\langle n' l' m' | \hat{x} \cdot \vec{e}_{\pm} | n l m \rangle = \sqrt{\frac{4\pi}{3}} \int d^3r \psi_{n'l'm'}^* r Y_{l', \pm 1}(\theta, \phi) \psi_{n l m}(r, \theta, \phi)$$

$$= \underbrace{\sqrt{\frac{4\pi}{3}} \int dr u_{n'l'}(r) r u_{nl}(r)}_{\text{Same radial integral as in part (b)} \int d\Omega Y_{l', \pm 1}^* Y_{l, \pm 1} Y_{lm}(\theta, \phi)$$

Same radial integral as in part (b) \equiv radial

The only difference now is the angular integral.

$$\text{Note: } \int d\Omega Y_{l', m'}^* Y_{l, \pm 1} Y_{l, m}(\theta, \phi) = \int d(\cos\theta) P_l^m(\cos\theta) P_l^{\pm 1}(\cos\theta) P_l^m(\cos\theta) \underbrace{\int_0^{2\pi} d\phi e^{i(m \pm 1 - m')\phi}}_{\delta_{m', m \pm 1}}$$

Thus there is a selection rule: For circularly oscillating field around z , the matrix element vanishes unless $m' = m \pm 1$

Consider thus the matrix elements between $|1s\rangle$ and $|2p, m = \pm 1\rangle$

$$\langle 2p, \pm 1 | \hat{x} \cdot \vec{e}_{\pm} | 1s \rangle = \text{radial} \int d\Omega Y_{l, \pm 1}^* Y_{l, \pm 1} (Y_{0,0}) = \frac{1}{\sqrt{4\pi}} = \frac{1}{\sqrt{4\pi}} \text{ radial} \\ \approx 0.75 \text{ e.d. } E_0 \text{ as before}$$

This problem is an example of the **Wigner-Eckart theorem**. Matrix elements of the form $\langle n l m | \hat{V} \cdot \vec{e}_{\mp} | n l m \rangle$ where \hat{V} is a "vector operator" and \vec{e}_{\mp} is a component \vec{e}_z, \vec{e}_{\pm} are all proportional to the same radial integral; all the angular components go into the overlap of spherical harmonics.

Problem 2: Matrix Elements in Hydrogen

(a) Consider the mean radius in a stationary state $|n, l, m\rangle$

$$\langle n, l, m | r | n, l, m \rangle = \int d^3r |\psi_{n, l, m}|^2 r = a_0 \underbrace{\int_0^\infty dr \bar{r} |U_{n, l}(\bar{r})|^2}_{\text{Radial integral (dimensionless)}}$$

Recall, the radial wavefunction: $U_{n, l}(\bar{r}) = N_{n, l} \bar{r}^{l+1} e^{-\frac{\bar{r}}{n}} \mathcal{L}_{n_r}^{2l+1}\left(\frac{2\bar{r}}{n}\right)$

where $N_{n, l} = \frac{2^{l+1}}{n^{l+2}} \sqrt{\frac{(n-l-1)!}{(n+l)!}}$ (normalization), $n_r = n - l - 1$: radial quantum number

$$\begin{aligned} \Rightarrow \langle r \rangle_{n, l} &= a_0 N_{n, l}^2 \int_0^\infty d\bar{r} \bar{r}^{2l+3} e^{-\frac{2\bar{r}}{n}} \left[\mathcal{L}_{n_r}^{2l+1}\left(\frac{2\bar{r}}{n}\right) \right]^2 \\ &= a_0 N_{n, l}^2 \left(\frac{n}{2}\right)^{2l+4} \underbrace{\int_0^\infty dx x^{2l+3} e^{-x} \left[\mathcal{L}_{n_r}^{2l+1}(x) \right]^2}_{\mathcal{I}} \quad \left(x = \frac{2\bar{r}}{n}\right) \end{aligned}$$

To solve for this integral the easiest approach is to use the generating function for the Laguerre polynomials

$$f_g(x, t) \equiv \sum_{n_r=0}^{\infty} t^{n_r} \mathcal{L}_{n_r}^g(x) = \frac{1}{(1-t)^{g+1}} e^{-\frac{t}{1-t}x}$$

$$\mathcal{L}_{n_r}^g(x) = \frac{1}{n_r!} \left. \frac{\partial^{n_r} f}{\partial t^{n_r}} \right|_{t=0}$$

$$\Rightarrow \mathcal{I} = \left. \frac{\partial^{n_r}}{\partial t_1^{n_r}} \frac{\partial^{n_r}}{\partial t_2^{n_r}} \right|_{t_1=t_2=0} \left[\frac{1}{[(1-t_1)(1-t_2)]^{g+1}} \int_0^\infty dx x^{2l+3} e^{-x} e^{-\frac{t_1 x}{1-t_1}} e^{-\frac{t_2 x}{1-t_2}} \right]$$

Aside $\int_0^\infty dx x^a e^{-bx} = a! \left(\frac{1}{b}\right)^{a+1}$, Here $a=2l+3$, $b = 1 + \frac{t_1}{1-t_1} + \frac{t_2}{1-t_2}$

Plugging all of this in, taking the derivatives and then the limit

$t_1, t_2 \rightarrow 0$ yields the result. $\langle r \rangle_{n, l} = a_0 \left(\frac{3}{2} n^2 - \frac{l(l+1)}{2} \right)$ phew!

For the ground state $\langle r \rangle_{1, 0} = \frac{3}{2} a_0$

The position of the peak probability for 1s is @ $|u_{1, 0}(r_{\text{max}})|^2 = a_0$

(b) We seek $\langle \frac{1}{r^3} \rangle_{nl}$. To find this we will use the Feynman-Hellman method.

Consider $\langle nlm | [\frac{\partial}{\partial r}, \hat{H}] | nlm \rangle = 0$ since $|nlm\rangle$ is an eigenstate of \hat{H}

$$\text{Aside: } \hat{H} = \frac{\hat{p}_r^2}{2m} + \underbrace{\frac{\hbar^2 l(l+1)}{2mr^2}}_{V_{\text{eff}}(r)} - \frac{e^2}{r^2}, \quad [\frac{\partial}{\partial r}, \hat{p}_r^2] = 0$$

$$[\frac{\partial}{\partial r}, V_{\text{eff}}(r)] \psi(r) = \frac{\partial}{\partial r} [V_{\text{eff}}(r) \psi(r)] - V_{\text{eff}} \frac{\partial \psi}{\partial r} = (\frac{\partial V_{\text{eff}}}{\partial r}) \psi(r)$$

$$\Rightarrow \langle nlm | [\frac{\partial}{\partial r}, \hat{H}] | nlm \rangle = \langle nlm | \frac{\partial V_{\text{eff}}}{\partial r} | nlm \rangle = - \langle nlm | (\frac{\hbar^2 l(l+1)}{mr^3} - \frac{e^2}{r^2}) | nlm \rangle = 0$$

$$\Rightarrow \frac{\hbar^2 l(l+1)}{m} \langle \frac{1}{r^3} \rangle_{nl} = e^2 \langle nlm | \frac{1}{r^2} | nlm \rangle$$

$$\Rightarrow \langle \frac{1}{r^2} \rangle_{nl} = \frac{mc^2}{\hbar^2} \frac{1}{l(l+1)} \langle \frac{1}{r^2} \rangle_{nl} = \frac{1}{a_0} \frac{1}{l(l+1)} \langle \frac{1}{r^2} \rangle_{nl}$$

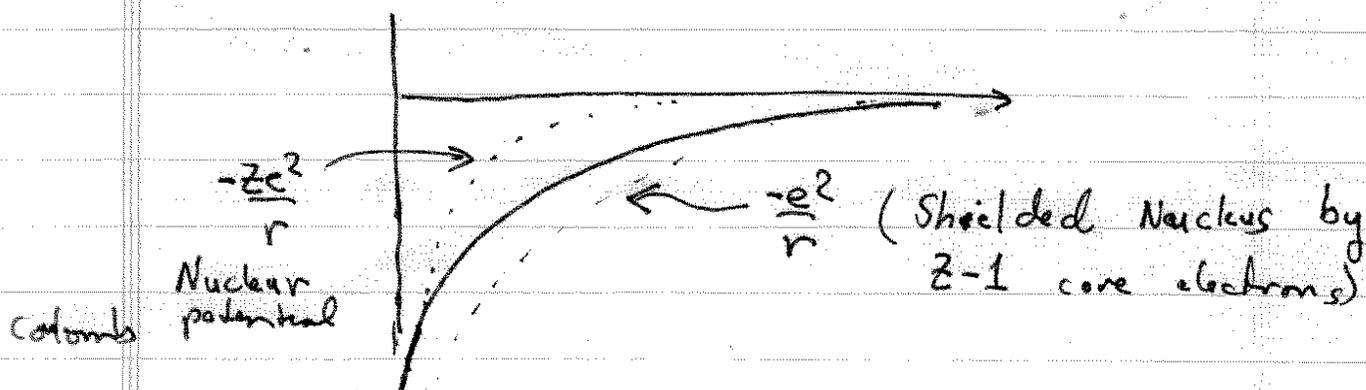
$$\text{From lecture, } \langle \frac{1}{r^2} \rangle_{nl} = \frac{1}{a_0^2} \frac{1}{n^3 (l + \frac{1}{2})}$$

$$\Rightarrow \langle \frac{1}{r^3} \rangle_{nl} = \frac{1}{a_0^3 n^3 (l + \frac{1}{2}) l(l+1)}$$

Problem 3: Spectrum of multielectron atoms

In the mean field approximation, we ignore electron correlations and then obtain a spherically symmetric charge distribution. The total potential seen by the valence electron is then the sum of the coulomb potential due to the attraction to the nucleus plus the repulsive potential due to the other "core" electrons

$$V(r) = V_{\text{nucleus}}(r) + V_{\text{core}}(r)$$



In a Bohr like picture for an alkali with one valence electron



The question is thus, how much does the wave function associated with the valence electron penetrate the core?

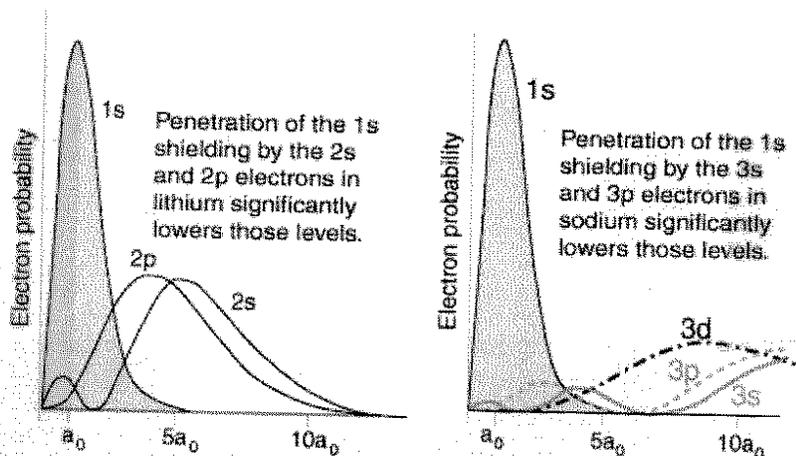
Since the potential is still spherically symmetric, the set $\{n, l, m\}$ are still "good quantum numbers". Because the radial wave functions associated with different l will have different support inside the core, the energy will be different. In particular, we expect the s -states ($l=0$) to have the lowest energy for a given n , since these are more peaked near the origin.

A nice description of this is given at the url:

<http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/orbdep.html>

Origin of Orbital Quantum Number Dependence of Electron Energies

When the wavefunctions for electrons with different orbital quantum numbers are examined, it is found that there is a different amount of penetration into the region occupied by the $1s$ electrons. This penetration of the shielding $1s$ electrons exposes them to more of the influence of the nucleus and causes them to be more tightly bound, lowering their associated energy states.



In the case of lithium, the $2s$ electron shows more penetration inside the first Bohr radius and is therefore lower than the $2p$. In the case of sodium with two filled shells, the $3s$ electron penetrates the inner shielding shells more than the $3p$ and is significantly lower in energy.

(b) Coarse but solvable model

$$V(r) = -\frac{e^2}{r} + \frac{A}{r^2}$$

Radial eq.

$$-\frac{1}{2} \frac{d^2 u}{d\bar{r}^2} + \left(\frac{l(l+1) + \bar{A}}{2\bar{r}^2} - \frac{1}{\bar{r}} \right) u = -\epsilon u$$

where $\bar{r} = \frac{r}{a_0}$ $\epsilon = -E / \frac{e^2}{a_0}$ binding energy
Bohr radius

$$\bar{A} = \frac{2A}{\hbar^2}$$

This is the same form of the radial equation as for Hydrogen, except $l(l+1) \rightarrow l(l+1) + \bar{A}$

Thus let $s(s+1) = l(l+1) + \bar{A}$

Making the Ansatz (as we did for Hydrogen)

$$u(\bar{r}) = \bar{r}^{s+1} e^{-K\bar{r}} F(\bar{r}) \quad K = \sqrt{2\epsilon}$$

We arrive at the Laguerre eq. with eigenfunction $L_{n_r}^{2s+1}(K\bar{r})$

Eigenvalue $K = \frac{1}{n_r + s + 1} = \sqrt{2\epsilon}$

$$\Rightarrow \epsilon = \frac{1}{2(n_r + s + 1)^2} \quad (\text{Next Page})$$

$$\rightarrow E = \frac{-R}{2(n_r + s + 1)^2} \quad R = \frac{e^2}{2a_0} = 13.6 \text{ eV}$$

Now we must solve for s in terms of l and A :

$$s^2 + s - (l(l+1) + \bar{A}) = 0$$

$$\Rightarrow s = -\frac{1}{2} + \frac{1}{2} \sqrt{1 + (4l(l+1) + \frac{8mA^2}{\hbar^2})}$$

↑
must choose (+)-sign to make $s > 0$

$$\Rightarrow s+1 = \frac{1}{2} \left(1 + \sqrt{(2l+1)^2 + \frac{8mA^2}{\hbar^2}} \right)$$

$$\therefore E_{n_r, l} = \frac{-R}{\left[n_r + \frac{1}{2} \left(1 + \sqrt{(2l+1)^2 + \frac{8mA^2}{\hbar^2}} \right) \right]^2}$$

Check $A \rightarrow 0$ $E_{n_r, l} = \frac{-R}{(n_r + l + 1)^2}$ as expected

Performing a power series expansion

$$E_{n_r, l} = \frac{-R}{(n_r + l + 1)^2} + \frac{R(2A)}{(n_r + l + 1)^3 (2l + 1)}$$

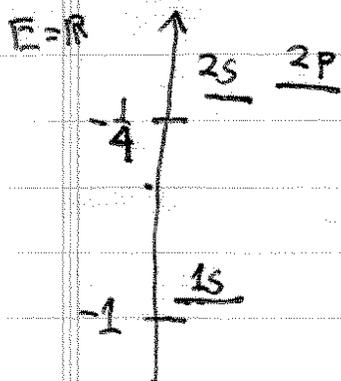
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Perturbation #

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⊙ In terms of principle q-number:

$$E_{n,l} = -\frac{R}{n^2} \left(1 - \frac{\bar{A}}{(l+\frac{1}{2})n} \right)$$

Sketch:



← degeneracy broken

2s is lower energy than 2p

Note $\frac{R\bar{A}}{n^3(l+\frac{1}{2})}$

follows from first order perturbation theory

$$E^{(1)} = \langle n,l | \frac{A}{r^2} | n,l \rangle = \frac{\hbar^2 \bar{A}}{2ma_0^2} \langle n,l | \frac{1}{r^2} | n,l \rangle$$

$$= R\bar{A} \frac{1}{n^3(l+\frac{1}{2})} \quad \text{as expected.}$$