1992 ϕ 507 Problems   Assigned: 3/23. Due: 3/30/92.   file $\mathcal{H}$9 (9)

(30) In stationary-state (non-degenerate) perturbation theory for $\mathcal{H}_0 \psi_k^{(0)} = E_k^{(0)} \psi_k^{(0)}$, the first-order correction to the system wavefunctions when $\mathcal{H}_0 \to \mathcal{H} = \mathcal{H}_0 + V$ is: $\psi_k^{(0)} \to \psi_k = \psi_k^{(0)} + \psi_k^{(1)}$, w/ $\psi_k^{(1)} = \sum_{n \neq k} a_{nk}^{(1)} \psi_n^{(0)}$, $a_{nk}^{(1)} = V_{nk}/(E_k^{(0)} - E_n^{(0)})$, $V_{nk} = \langle n|V|k\rangle$. Show that this ψ_k, correct to $\mathcal{O}(V)$, is sufficient to give an energy correct to $\mathcal{O}(V^2)$ by calculating: $E_k = \langle \psi_k|\mathcal{H}|\psi_k\rangle / \langle \psi_k|\psi_k\rangle$.

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(31) [15pts, ~Davydov #5, p.205]. The proton has a finite size; its (rms) radius: $R_p \simeq 0.8 \times 10^{-13}$ cm. At distances $r \sim R_p$ the e-p interaction is thus not Coulombic, but is modified to: $-e^2/r + U(r)$, w/ $U(r)$ the perturbation due to the proton charge distribution. $U(r)$ shifts the hydrogen atom energy levels E_n by small amounts.

(A) Assume the proton is a uniformly charged spherical shell of radius R_p. Show that the $n S_{1/2}$ state energies shift by: $\Delta E_n \simeq \frac{4}{3}(Z^2/n)[R_p/a_0]^2 |E_n|$, E_n = Bohr energy.

(B) What is ΔE_n of part (A) if the proton is a uniformly charged sphere of radius R_p?

(C) How big is ΔE_n (comparatively) for states with ∡ momentum $l > 0$?

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(32) The Stark Effect on the ground state of hydrogen perturbs the energy $E_0^{(0)}$ to $\mathcal{O}(\mathcal{E}^2)$ as: $E_0 = E_0^{(0)} - e^2 \mathcal{E}^2 S_z$, where: $S_z = \sum_{n>0} |\langle n|z|0\rangle|^2 / (E_n^{(0)} - E_0^{(0)})$, for a field $\vec{\mathcal{E}}$ along the z-axis. We showed in class that the sum was just: $S_z = -\langle 0|zF|0\rangle$, if a function F could be found such that: $z|0\rangle = [F, \mathcal{H}_0]|0\rangle$, w/ $\mathcal{H}_0$ = unperturbed Hamiltonian. Assume: $F = (ma^2/\hbar^2)(\lambda\rho + \mu)z$, w/ $a = \hbar^2/me^2$, $\rho = r/a$, $z = r\cos\theta$, and λ & μ = numerical coefficients to be found. Find λ & μ by writing out the differential eqtn for F, and show: $F = -(ma/2\hbar^2)(r + 2a)z$, as was used in class.

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(33) [Schmidt orthogonalization]. Consider an N-fold set of eigenfcns $\{u_i\}$, $1 \leq i \leq N$, that are degenerate (each has same eigenenergy E: $\mathcal{H} u_i = E u_i$), and not orthogonal: $\langle u_i|u_j\rangle \neq 0$. We want a set $\{v_k\}$, constructed from linear comb$^{\text{n}}$s of the u_i, which is orthogonal.

(A) Start with $v_1 = u_1$. Set $v_2 = u_2 + a_{21} v_1$ and find a_{21} such that $\langle v_1|v_2\rangle = 0$. Next, set $v_3 = u_3 + a_{31} v_1 + a_{32} v_2$, and find a_{31} & a_{32} such that $\langle v_1|v_3\rangle = 0$ & $\langle v_2|v_3\rangle = 0$.

(B) Show by induction that the n^{th} member of the orthogonal set $\{v_k\}$ is, for $n > 1$: $v_n = u_n - \sum_{k=1}^{n-1} (\langle v_k|u_n\rangle / \langle v_k|v_k\rangle) v_k$.

In SS(ND)PT, find E to $\mathcal{O}(V^2)$ from ψ to $\mathcal{O}(V)$.

1. Given: $\psi_k = \psi_k^{(0)} + \sum_{n\neq k} a_{nk}^{(1)}\psi_n^{(0)}$, $a_{nk}^{(1)} = V_{nk}/(E_k^{(0)} - E_n^{(0)})$ & $V_{nk} = \langle \underset{\psi_n^{(0)}}{n}|V|\underset{\psi_k^{(0)}}{k}\rangle$,

we wish to calculate the (perturbed) energy E_k in state k via:

$$\rightarrow E_k = \langle\psi_k|\mathcal{H}|\psi_k\rangle/\langle\psi_k|\psi_k\rangle, \text{ w/ } \mathcal{H} = \mathcal{H}_0 + V. \qquad (1)$$

So/ $$\underline{\underline{\text{DENOM.}}} = \langle \psi_k^{(0)} + \sum_m{}' a_{mk}^{(1)}\psi_m^{(0)} | \psi_k^{(0)} + \sum_n{}' a_{nk}^{(1)}\psi_n^{(0)}\rangle = 1 + \sum_n{}' |a_{nk}^{(1)}|^2. \qquad (2)$$

This employs orthonormality: $\langle\psi_m^{(0)}|\psi_n^{(0)}\rangle = \delta_{mn}$. Numerator is messier...¶

$$\underline{\underline{\text{NUMER.}}} = \langle \psi_k^{(0)} + \sum_m{}' a_{mk}^{(1)}\psi_m^{(0)} | \mathcal{H}_0 + V | \psi_k^{(0)} + \sum_n{}' a_{nk}^{(1)}\psi_n^{(0)}\rangle \qquad (3)$$

$$= E_k^{(0)} + V_{kk} + \sum_n{}' a_{nk}^{(1)}\langle k|\mathcal{H}_0 + V|n\rangle + \sum_m{}' a_{mk}^{(1)*}\langle m|\mathcal{H}_0 + V|k\rangle +$$

$$+ \sum_{m,n}{}' a_{mk}^{(1)*} a_{nk}^{(1)} \langle m|\mathcal{H}_0 + \overset{\mathcal{O}(V^3)}{\cancel{V}}|n\rangle \leftarrow \text{now drop } \mathcal{O}(V^3) \text{ terms...}$$

$$= E_k^{(0)} + V_{kk} + \sum_n{}' a_{nk}^{(1)} V_{kn} + \sum_m{}' a_{mk}^{(1)*} V_{mk} + \sum_{m,n}{}' a_{mk}^{(1)*} a_{nk}^{(1)} E_n^{(0)}\delta_{mn}$$

$$= E_k^{(0)} + V_{kk} + 2\sum_n{}' \frac{|V_{nk}|^2}{E_k^{(0)} - E_n^{(0)}} + \sum_n{}' \frac{|V_{nk}|^2}{(E_k^{(0)} - E_n^{(0)})^2} E_n^{(0)}, \text{ after putting in: } a_{nk}^{(1)} = V_{nk}/(E_k^{(0)} - E_n^{(0)}).$$

or/ $$\underline{\text{NUMER.}} = E_k^{(0)} + V_{kk} + \sum_n{}' \left(2 + \frac{E_n^{(0)}}{E_k^{(0)} - E_n^{(0)}}\right)\frac{|V_{nk}|^2}{E_k^{(0)} - E_n^{(0)}}, \text{ after rearranging terms.} \qquad (4)$$

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2. Now form E_k of Eq.(1) as: $E_k = (\text{NUMER.})/(\text{DENOM.})$, and drop all terms of $\mathcal{O}(V^3)$ and higher. Thus: $1/(\text{DENOM.}) = 1 - \sum_n{}' |a_{nk}^{(1)}|^2$, to $\mathcal{O}(V^2)$, and...

$$E_k = \frac{\text{NUMER.}}{\text{DENOM.}} = E_k^{(0)}\left(1 - \sum_n{}' |a_{nk}^{(1)}|^2\right) + V_{kk} + \sum_n{}' \left(1 + \frac{E_k^{(0)}}{E_k^{(0)} - E_n^{(0)}}\right)\frac{|V_{nk}|^2}{E_k^{(0)} - E_n^{(0)}},$$

cancel

or/ $$\boxed{E_k = E_k^{(0)} + V_{kk} + \sum_n{}' \frac{|V_{nk}|^2}{E_k^{(0)} - E_n^{(0)}}}, \text{ to } \mathcal{O}(V^2). \qquad (5)$$

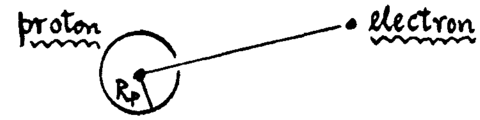
This result for E_k is correct to terms of $\mathcal{O}(V^2)$, per Davydov Eq. (47.11), or class notes, Eq. (26b), p. SS9.

¶ $\langle k|\mathcal{H}|n\rangle \equiv \langle\psi_k^{(0)}|\mathcal{H}|\psi_n^{(0)}\rangle$; $\sum_m{}' \equiv \sum_{m\neq k}$, etc. is the notation.

(1) [15 pts ($\sim$ Davydov #5, p. 205)]. Calculate $nS_{1/2}$-level energy shift due to finite proton size.

(A) 1. For proton models with a sharp boundary at radius R_p, the e-p interaction is:

$$\rightarrow V(r) = \begin{cases} -e^2/r, \text{ for } r > R_p; \\ -e^2/r + U(r), \; r \leq R_p. \end{cases} \quad (1)$$



The perturbation $U(r)$ depends on the specific proton model, but it will always be "small", because $U(r)$ is nonzero only over dimensions $R_p \sim 10^{-5} a_0$, a_0 = Bohr radius $\sim$ atomic dimension. As we shall see below, the fractional energy shift is $\propto (R_p/a_0)^2 \sim 10^{-10}$. A 1st order perturbation is adequate to handle this correction, and it prescribes an energy shift (upward, because e-p binding is weakened) of size

$$\rightarrow \Delta E = \int_\infty d^3x \, |\Psi(\vec{r})|^2 U(r) = 4\pi \int_0^{R_p} |\psi(r)|^2 U(r) r^2 dr, \quad (2)$$

in the state Ψ. Since $U(r)$ depends only on the radial distance r, and is zero at $r > R_p$, we have done the $\measuredangle$ integration (leaving $\psi(r)$ as the radial part of $\Psi(\vec{r})$), and have truncated the r-integration

2. Now since $a_0 \gg R_p$ is the scale length for $\psi(r)$, then over $0 \leq r \leq R_p$, $\psi(r)$ is very little different from $\psi(0)$ in the integral in (2). We thus extract $|\psi(r)|^2 \simeq |\psi(0)|^2$ from the integral and label it with the Bohr quantum # n. Then...

$$\boxed{\Delta E_n = 4\pi |\psi_n(0)|^2 \int_0^{R_p} r^2 U(r) dr.} \quad (3)$$

Non-relativistically, $|\psi_n(0)|^2 \equiv 0$ in all but $nS_{1/2}$ states of the H-like atom. In the $nS_{1/2}$ states, we have: $|\psi_n(0)|^2 = \frac{1}{\pi}(Z/na_0)^3$, w/ $Z=1$ for hydrogen.

3. For a spherical shell proton model, evidently

$$\rightarrow U(r) = \begin{cases} (e^2/r - e^2/R_p), \; 0 \leq r \leq R_p, \\ 0, \text{ for } r > R_p; \end{cases} \text{ so...} \rightarrow \int_0^{R_p} r^2 U(r) dr = \frac{1}{6} e^2 R_p^2. \quad (4)$$

Then, for this proton model, the energy shift due to finite p-size is, by (3) insert Z here if nuclear charge is Ze instead of e.

$$\underline{\underline{\Delta E_n = \frac{2}{3}\pi e^2 R_p^2 |\psi_n(0)|^2}}, \text{ for spherical shell proton.} \qquad (5)$$

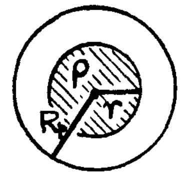
Put in $|\psi_n(0)|^2$ here, and normalize to Bohr energy $|E_n| = (Ze)^2/2n^2 a_0$, so...

$$\rightarrow \boxed{\Delta E_n/|E_n| = \frac{4}{3}(Z^2/n)(R_p/a_0)^2}, \text{ for } nS_{1/2} \text{ levels.} \qquad (6)$$

The fractional proton size correction is $\sim (R_p/a_0)^2$, as asserted above. For $n=2$ and $R_p = 0.8 \times 10^{-13}$ cm: $\Delta E_2 = 0.126$ MHz. The shift is small, but detectable, since the $2S_{1/2} - 2P_{1/2}$ separation (Lamb shift $\mathcal{S}$) has been measured to a (1σ) accuracy of ± 0.020 MHz†. <u>NOTE</u>: the $2P_{1/2}$ level is virtually unshifted by the size correction, since it is an $l=1$ state with $|\psi_n(0)|^2 \equiv 0$. See remarks in part (C).

<u>4.</u> For a proton model of a radially symmetric sphere of radius R_p, potential @ $r \leq R_p$ is:

(B) $$\rightarrow V(r) = -\frac{e^2}{R_p} + e\int_{R_p}^{r} \underbrace{E(x)}_{\text{electric field}} dx, \quad \text{w/ } E(x) = \frac{4\pi}{x^2}\int_0^x u^2 \underbrace{\rho(u)}_{\text{charge density}} du. \qquad (7)$$



The perturbation due to finite proton size is then...

$$\rightarrow U(r) = V(r) + \frac{e^2}{r} = \left(\frac{e^2}{r} - \frac{e^2}{R_p}\right) - e\int_{r \leq R_p}^{R_p} \left\{ \frac{4\pi}{x^2}\int_0^x u^2 \rho(u)\, du \right\} dx. \qquad (8)$$

For a uniformly charged sphere: $\rho = e/\frac{4\pi}{3}R_p^3 = $ cnst, so: $\frac{4\pi}{x^2}\int_0^x u^2 \rho\, du = ex/R_p^3$,

and// $$U(r) = \left(\frac{e^2}{r} - \frac{e^2}{R_p}\right) - \frac{e^2}{2R_p}\left(1 - \frac{r^2}{R_p^2}\right), \text{ for uniform sphere;} \qquad (9)$$

So// $$\int_0^{R_p} r^2 U(r)\, dr = \frac{1}{10} e^2 R_p^2 \quad \Rightarrow \underline{\underline{\Delta E_n = \frac{2}{5}\pi e^2 R_p^2 |\psi_n(0)|^2}}, \text{ by Eq. (3)} \qquad (10)$$

Comparison of (5) & (10) shows (for $nS_{1/2}$ states): $\Delta E_n \left(\begin{smallmatrix}\text{uniform}\\ \text{sphere}\end{smallmatrix}\right) = \frac{3}{5}\left(\begin{smallmatrix}\text{spherical}\\ \text{shell}\end{smallmatrix}\right)$.

(C) <u>5.</u> For H-atom states with $l > 0$ and $\rho = r/a_0 \ll 1$, $\psi_{nl}(r) \simeq N_{nl}\left(\frac{Z\rho}{n}\right)^l$, w/ N_{nl} = norm cnst. Aside from numerical factors ~ 1, the integrand in Eq. (3) picks up an additional factor of $(r/a_0)^{2l}$, and--approximately-- <u>the shift ΔE_n is reduced by a factor $\sim (R_p/a_0)^{2l}$</u>. Since $(R_p/a_0) \sim 10^{-5}$, this renders ΔE_n negligible (w.r.t. $nS_{1/2}$) for $l > 0$ states.

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† R.T. Robiscoe & T.W. Shyn, Phys. Rev. Letters <u>24</u>, 559 (1970).

ϕ507 Solutions

(32) For hydrogen ground state, find fcn F such that : $z|0\rangle = [F, \mathcal{H}_0]|0\rangle$.

1. Hamiltonian is : $\mathcal{H}_0 = -\frac{\hbar^2}{2mr^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \hat{\Lambda}\right] - (e^2/r)$, per Davydov Eq. (34.2), and : $\mathcal{H}_0|0\rangle = E_0^{(0)}|0\rangle$, w/ $E_0^{(0)} = -e^2/2a$, $a = \hbar^2/me^2$. Eqtn defining F is then

$$\rightarrow z|0\rangle = F\mathcal{H}_0|0\rangle - \mathcal{H}_0 F|0\rangle$$

$$= -\frac{e^2}{2a}F|0\rangle + \frac{\hbar^2}{2mr^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \hat{\Lambda}\right]F|0\rangle + (e^2/r)F|0\rangle \qquad (1)$$

$|0\rangle = e^{-r/a}$ for the ground state [norm cnst cancels out of (1)], and $\hat{\Lambda}$ does nothing to this spherically symmetric state. Then, with $\rho = r/a$, Eq. (1) requires

$$\rightarrow z = \frac{\hbar^2}{2ma^2}\frac{1}{\rho^2}\Big[\underbrace{e^{\rho}\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial}{\partial\rho}\right)Fe^{-\rho}}_{\text{simplifies to : } \rho^2\frac{\partial}{\partial\rho}\left(\frac{\partial F}{\partial\rho} - F\right) + (2\rho - \rho^2)\left(\frac{\partial F}{\partial\rho} - F\right).} + \hat{\Lambda}F\Big] + \frac{e^2}{a}\left(\frac{1}{\rho} - \frac{1}{2}\right)F \qquad (2)$$

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2. Now choose : $F = \frac{ma^2}{\hbar^2}(\lambda\rho + \mu)z$, λ & μ = numerical cnsts to be found, and $z = r\cos\theta$. Since $\cos\theta = P_\ell(\cos\theta)|_{\ell=1}$ is an ∡lar mom. eigenfcn, then by Davydov Eq. (34.3) [also (16.18) & (8.10)] : $\Lambda\cos\theta = -\ell(\ell+1)\cos\theta|_{\ell=1}$. Using this in (2), plus...

$$\left(\frac{\partial F}{\partial\rho} - F\right) = \frac{ma^2}{\hbar^2}\left[\mu + (2\lambda - \mu)\rho - \lambda\rho^2\right]a\cos\theta \qquad (3)$$

used : $z = \rho a\cos\theta$, here...

so//

$$\text{Eq. (2)} \Rightarrow \rho = \frac{1}{2\rho^2}\left\{\rho^2\left[(2\lambda - \mu) - 2\lambda\rho\right] + (2\rho - \rho^2)\left[\mu + (2\lambda - \mu)\rho - \lambda\rho^2\right] - 2(\lambda\rho + \mu)\rho\right\} +$$

$$+ \left[\cancel{\frac{e^2}{a}\cdot\frac{ma^2}{\hbar^2}}^{\,1}\right]\left(1 - \frac{\rho}{2}\right)(\lambda\rho + \mu)$$

have cancelled $a\cos\theta$ throughout

or//

$$\rightarrow 2\rho^3 = 2(2\lambda - \mu)\rho^2 - 4\lambda\rho^3, \text{ after collecting terms on RHS.} \qquad (4)$$

This equality is satisfied for the choice : $\underline{\underline{\lambda = -\frac{1}{2},\ \mu = 2\lambda = -1}}$. Hence :

$$\boxed{F = (-)\frac{ma}{2\hbar^2}(r + 2a)z} \quad \text{w/ } a = \hbar^2/me^2,\ z = r\cos\theta. \qquad (5)$$

This F satisfies : $z|0\rangle = [F, \mathcal{H}_0]|0\rangle$ w.r.t. the H-atom ground state.

● Schmidt Orthogonalization: Construct orthogonal set $\{v_k\}$ from nonorthogonal $\{u_i\}$.

1. With $v_1 = u_1$, and $v_2 = u_2 + a_{21} v_1$, orthogonal of v_2 & v_1 requires...

$$\rightarrow \langle v_1 | v_2 \rangle = \langle u_1 | u_2 \rangle + a_{21} \langle u_1 | u_1 \rangle = 0 \Rightarrow \underline{\underline{a_{21} = -\langle v_1 | u_2 \rangle / \langle v_1 | v_1 \rangle}}. \quad (1)$$

Now, if: $v_3 = u_3 + a_{31} v_1 + a_{32} v_2$, orthogonality of v_3 & v_1 and v_3 & v_2 $\Rightarrow$

$$\langle v_1 | v_3 \rangle = \langle v_1 | u_3 \rangle + a_{31} \langle v_1 | v_1 \rangle + a_{32} \cancelto{0}{\langle v_1 | v_2 \rangle} = 0, \text{ so } \underline{\underline{a_{31}}} = -\frac{\langle v_1 | u_3 \rangle}{\langle v_1 | v_1 \rangle}; \quad (2)$$

$$\langle v_2 | v_3 \rangle = \langle v_2 | u_3 \rangle + a_{31} \cancelto{0}{\langle v_2 | v_1 \rangle} + a_{32} \langle v_2 | v_2 \rangle = 0, \text{ so } \underline{\underline{a_{32}}} = -\frac{\langle v_2 | u_3 \rangle}{\langle v_2 | v_2 \rangle}. \quad (3)$$

The pattern that emerges from Eqs. (1)-(3) is that if v_n is written in form:

$$v_n = u_n + \sum_{k=1}^{n-1} a_{nk} v_k, \quad n > 1 \ (\text{and } v_1 = u_1),$$

$$\text{then } \langle v_l | v_n \rangle = 0 \text{ for } l = 1, 2, \ldots, n-1, \ \underline{\text{if}}: \underline{\underline{a_{nk}}} = (-) \frac{\langle v_k | u_n \rangle}{\langle v_k | v_k \rangle}. \quad (4)$$

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2. Consider an induction on the proposition in Eq. (4). Proposition is true for the first nontrivial n (viz. $n=2$). We want to show that assuming proposition is true for some general n ($n>2$) allows us to prove it is true for $(n+1)$. That is...

Assume: $v_n = u_n + \sum_{k=1}^{n-1} a_{nk} v_k$, is $\perp$ all v_l for $l = 1, 2, \ldots, n-1$ (i.e. $\langle v_l | v_n \rangle \equiv 0$).

Then show: $v_{n+1} = u_{n+1} + \sum_{k=1}^{n} a_{n+1,k} v_k$, is $\perp$ all v_m for $m = 1, 2, \ldots n$. (5)

For $m=n$, have: $\langle v_n | v_{n+1} \rangle = \langle v_n | u_{n+1} \rangle + a_{n+1,n} \langle v_n | v_n \rangle$, since $\langle v_n | v_k \rangle \equiv 0$ for all $k = 1, 2, \ldots, n-1$ (by assumption). Put in $a_{n+1,n}$ from Eq. (4), to see $\langle v_n | v_{n+1} \rangle \equiv 0$. Then, for $m = l$, w/ $l = 1, 2, \ldots, n-1$, calculate the projection...

$$\rightarrow \langle v_l | v_{n+1} \rangle = \langle v_l | u_{n+1} \rangle + \sum_{k=1}^{n} a_{n+1,k} \overbrace{\langle v_l | v_k \rangle}^{\text{nonzero only for } k=l.} = \langle v_l | u_{n+1} \rangle + a_{n+1,l} \langle v_l | v_l \rangle. \quad (6)$$

Again, putting in $a_{n+1,l}$ from Eq. (4), we see $\langle v_l | v_{n+1} \rangle \equiv 0$. Hence $\langle v_m | v_{n+1} \rangle$ is $\perp$ all the v_m for $m = 1, 2, \ldots, n$. Proposition in (5) is true, so (4) is correct by induction.