(25) [15 pts.] Phase shift analysis for hard-core scattering (class notes, pp. PW 10-12) requires knowing the radial wavefcn logarithmic derivative $R'_{k\ell}(a)/R_{k\ell}(a)$ at the cutoff $r=a$ of the scattering potential. Consider the <u>dimensionless</u> logarithmic derivative: $\beta_\ell(k) = a\,R'_{k\ell}(a)/R_{k\ell}(a)$. We wish to find how $\beta_\ell(k)$ depends on energy.

(A) For a given ∡ momentum ℓ, consider two closely spaced energies: E_1 & $E_2 = E_1+\Delta E$. If $R_1 = R_{k_1\ell}(r)$ & $R_2 = R_{k_2\ell}(r)$ are the corresponding interior radial wavefcns, show that: $\underline{\frac{d}{dr}\left[r^2(R_1R_2' - R_2R_1')\right] + \frac{2m}{\hbar^2}(E_2-E_1)r^2R_1R_2 = 0}$. [HINT: write the radial eqtns for R_1 & R_2 from Eq.(26), p. PW 8. Recall: $k^2 = 2mE/\hbar^2$. Then, think Green].

(B) Integrate the identity in part (A) over $0 \leq r \leq a$ to find an expression for $\Delta\beta_\ell/\Delta E = [\beta_\ell(k_2) - \beta_\ell(k_1)]/(E_2-E_1)$. Pass to the limit $k_2 \to k_1 = k$ to derive the expression: $\underline{\underline{d\beta_\ell(k)/dE = -(2m/\hbar^2 a)\int_0^a [r R_{k\ell}(r)/R_{k\ell}(a)]^2 dr}}$. So, how <u>does</u> $\beta_\ell(k)$ vary w/ E?

---

(26) (A) Find the exchange splitting of an energy level in a system of two electrons, by regarding the e-e interaction $V(\mathbf{r}_1-\mathbf{r}_2)$ as a perturbation on the main electron binding terms. Use appropriate <u>symmetrized</u> wavefcns for the electrons.

(B) Show that the exchange-dependent terms in part (A) can be represented w.r.t. <u>non-symmetrized</u> electron spin states (i.e. product states) as eigenvalues of the exchange operator: $\underline{V_{ex} = -\frac{K}{2}(1+4\sigma_1\cdot\sigma_2)}$. Here, K is the exchange integral from part (A), and σ_1 and σ_2 are the (dimensionless) spin operators for electrons #1 & 2.

---

(27) [15 pts.]. Employ $a_0 = \frac{\hbar^2}{me^2}$ (Bohr radius) as a length unit, and $E_0 = \frac{e^2}{a_0}$ (2× H atom ionization) as an energy unit. Using the Thomas-Fermi model, estimate the <u>average</u> size of the following quantities [what's interesting is the scaling with Z]: (A) distance of an electron from the nucleus, (B) Coulomb interaction energy between two electrons, (C) kinetic energy of an electron, (D) energy needed to ionize the atom completely, (E) velocity of an electron in the atom, (F) angular momentum of an electron, (G) radial quantum number of an electron.

ϕ507 Solutions

(25) [15 pts.]. Analyse energy dependence of the log derivative $\beta_\ell(k) = \frac{a}{R_{k\ell}} R_{k\ell}'|_{r=a}$.

1. From class notes p. PW 8, Eq. (26), the radial eqtns for R_1 & R_2 are

(A)
$$\rightarrow \left[\frac{d^2}{dr^2} + k_\lambda^2 - \frac{\ell(\ell+1)}{r^2}\right](r R_\lambda) = \left[\frac{2mV(r)}{\hbar^2}\right](r R_\lambda) \quad \left\{ \begin{array}{l} \lambda = 1, 2; \text{ and...} \\ \text{energies}: E_\lambda = \hbar^2 k_\lambda^2/2m. \end{array}\right. \tag{1}$$

Form the quantity: $rR_1 \cdot [\text{Eq.}(1): \lambda = 2] - rR_2 \cdot [\text{Eq.}(1): \lambda = 1]$, to obtain...

$$\rightarrow \left[(rR_1)\cdot \frac{d^2}{dr^2}(rR_2) - (rR_2)\cdot \frac{d^2}{dr^2}(rR_1)\right] + (k_2^2 - k_1^2) r^2 R_1 R_2 = 0. \tag{2}$$

It is straightforward to establish an identity for the [ ] in Eq. (2), viz.

$$\rightarrow [\text{Eq.}(2)] = \frac{d}{dr}\left[r^2\left(R_1 \frac{dR_2}{dr} - R_2 \frac{dR_1}{dr}\right)\right], \tag{3}$$

and so, with $k_\lambda^2 = 2mE_\lambda/\hbar^2$, Eq. (2) reads...

$$\frac{d}{dr}\left[r^2\left(R_1 \frac{dR_2}{dr} - R_2 \frac{dR_1}{dr}\right)\right] + \frac{2m}{\hbar^2}(E_2 - E_1) r^2 R_1 R_2 = 0. \tag{4}$$

---

2. Integrate through Eq. (4) by $\int_0^a dr \cdot$, then divide by $R_1(a) R_2(a)$...

(B)
$$\rightarrow a^2\left(R_1 \frac{dR_2}{dr} - R_2 \frac{dR_1}{dr}\right)\Big|_{r=a} + \frac{2m}{\hbar^2}(E_2 - E_1)\int_0^a r^2 R_1(r) R_2(r)\, dr = 0,$$

or
$$\left[\underbrace{\frac{a}{R_2}\left(\frac{dR_2}{dr}\right)}_{\beta_\ell(k_2)} - \underbrace{\frac{a}{R_1}\left(\frac{dR_1}{dr}\right)}_{\beta_\ell(k_1)}\right]_{r=a} = -\frac{2m}{\hbar^2 a}(E_2 - E_1)\frac{1}{R_1(a) R_2(a)}\int_0^a r^2 R_1(r) R_2(r)\, dr$$

So,
$$\frac{\Delta \beta_\ell}{\Delta E} = \frac{\beta_\ell(k_2) - \beta_\ell(k_1)}{E_2 - E_1} = -\frac{2m/\hbar^2 a}{R_1(a) R_2(a)}\int_0^a r^2 R_1(r) R_2(r)\, dr. \tag{5}$$

As $k_2 \rightarrow k_1+$, the LHS of (5) becomes $d\beta_\ell/dE$, and $R_2 \rightarrow R_1$ on RHS. So...

$$\boxed{\frac{d\beta_\ell}{dE} = -\left(\frac{2m}{\hbar^2 a}\right)\int_0^a r^2 [R_{k\ell}(r)/R_{k\ell}(a)]^2\, dr < 0}. \tag{6}$$

This holds at any k-value, and shows that $\beta_\ell(k)$ is a <u>monotonically decreasing</u> fcn of the energy E.

(26) Exchange splitting for a 2e system. Representation via an exchange potential.

(A) 1. The electrons have spin $\sigma_1 = \frac{1}{2} = \sigma_2$, and appear in total spin states: $\sigma = \sigma_1 + \sigma_2 = 1$ (spin triplet, w/ even exchange symmetry), and $\sigma = \sigma_1 + \sigma_2 = 0$ (spin singlet, w/ odd exchange symmetry). The corresponding space states are of opposite symmetry:

$$\rightarrow \psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \begin{cases} \phi_\alpha(\mathbf{r}_1)\phi_\beta(\mathbf{r}_2) - \phi_\beta(\mathbf{r}_1)\phi_\alpha(\mathbf{r}_2) = \psi_T(\mathbf{r}_1,\mathbf{r}_2), \text{ for } \sigma = 1 \text{ (triplet)}; \\ \phi_\alpha(\mathbf{r}_1)\phi_\beta(\mathbf{r}_2) + \phi_\beta(\mathbf{r}_1)\phi_\alpha(\mathbf{r}_2) = \psi_S(\mathbf{r}_1,\mathbf{r}_2), \text{ for } \sigma = 0 \text{ (singlet)}. \end{cases} \quad (1)$$

2. If the e-e interaction $V(\mathbf{r}_1 - \mathbf{r}_2)$ is a perturbation, then the energy shift is ...

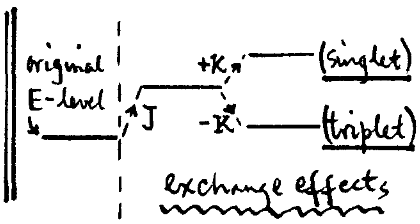
$$\rightarrow \langle V \rangle = \langle \psi | V | \psi \rangle = \begin{cases} \langle \psi_T | V | \psi_T \rangle = V_T, \text{ for } \sigma = 1 \text{ (triplet)}, \\ \langle \psi_S | V | \psi_S \rangle = V_S, \text{ for } \sigma = 0 \text{ (singlet)}; \end{cases} \quad (2)$$

in lowest order. We calculate ...

$$\left[\begin{aligned} V_T &= \tfrac{1}{2}\langle \phi_\alpha(1)\phi_\beta(2) - \phi_\beta(1)\phi_\alpha(2) | V | \phi_\alpha(1)\phi_\beta(2) - \phi_\beta(1)\phi_\alpha(2) \rangle = J - K, \\ V_S &= \tfrac{1}{2}\langle \phi_\alpha(1)\phi_\beta(2) + \phi_\beta(1)\phi_\alpha(2) | V | \phi_\alpha(1)\phi_\beta(2) + \phi_\beta(1)\phi_\alpha(2) \rangle = J + K; \end{aligned}\right\} \quad (3)$$

w/ $J = \langle \phi_\alpha(1)\phi_\beta(2) | V(\mathbf{r}_1 - \mathbf{r}_2) | \phi_\alpha(1)\phi_\beta(2) \rangle$ ← direct integral (4A)

$\rightarrow K = \langle \phi_\alpha(1)\phi_\beta(2) | V(\mathbf{r}_1 - \mathbf{r}_2) | \phi_\beta(1)\phi_\alpha(2) \rangle$ ← exchange integral (4B)



We've assumed $V(\mathbf{r}_2 - \mathbf{r}_1) \equiv V(\mathbf{r}_1 - \mathbf{r}_2)$, which is of course true for the e-e interaction. The singlet-triplet splitting ends up as $(E+J) \pm K$, w/ $K \Rightarrow$ exchange effects.

(B) 3. Consider the exchange potential: $V_{ex} = -\frac{1}{2}K(1 + 4\,\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2)$. Its eigenvalues for product states $\phi_\alpha(1)\phi_\beta(2)|\sigma, m_s\rangle$ containing eigenfcns $|\sigma, m_\sigma\rangle$ of total spin will be:

$$\underline{\langle V_{ex} \rangle = -\tfrac{1}{2}K(1 + 4\langle \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 \rangle)}, \quad \langle \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 \rangle = \text{expectation value w.r.t.} \begin{cases} \text{singlet } (\sigma = 0), \\ \text{triplet } (\sigma = 1). \end{cases} \quad (5)$$

But total spin $\boldsymbol{\sigma} = \boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2$, so $\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 = \frac{1}{2}[\boldsymbol{\sigma}^2 - \boldsymbol{\sigma}_1^2 - \boldsymbol{\sigma}_2^2]$. For QM expectation values:

$$\left[\ \langle \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 \rangle = \tfrac{1}{2}[\sigma(\sigma+1) - \sigma_1(\sigma_1+1) - \sigma_2(\sigma_2+1)]; \text{ w/ } \sigma_1 = \tfrac{1}{2} = \sigma_2, \ \& \ \sigma = 0, 1.\right.$$

So $\underline{\langle \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 \rangle = -\frac{3}{4}}$, for $\sigma = 0$; $\underline{\langle \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 \rangle = +\frac{1}{4}}$, for $\sigma = 1 \Rightarrow$ $\boxed{\begin{aligned} \langle V_{ex} \rangle &= +K \ \left(\text{for } \sigma = 0 \text{ singlet}\right), \\ &= -K \ \left(\text{for } \sigma = 1 \text{ triplet}\right). \end{aligned}}$ (6)

$\langle V_{ex} \rangle$ neatly accounts for the exchange splitting in Eq. (3).

ϕ507 Solutions

(27) [15 pts]. Average sizes in the TF (Thomas-Fermi) atom: scaling with Z.

(A) The length scale in the TF atom is [class notes: p. ip 17, Eq.(42)]: $b = 0.885 \frac{a_0}{Z^{1/3}}$. The atom is not more than a few × b in size (graph of $\phi(x)$ on p. ip 18). Put the numerical factor $0.885 \sim 1$; it is reasonable to claim that the average distance of an electron from the nucleus in a TF atom is: $\boxed{r_e \sim Z^{-\frac{1}{3}} a_0}$.

(B) e-e interaction: $V_{ee} \sim e^2/r_e$, w/ $\boxed{V_{ee} \sim Z^{1/3} e^2/a_0}$.

(C) An electron can have a maximum K.E. $= \frac{1}{2m} p_{max}^2 = -U(r) = \frac{Ze^2}{b}\left[\frac{1}{x}\phi(x)\right]$, by the remarks on pp. ip 16-17. The average K.E. will be some fraction of this; i.e. of order: $K_e \sim Ze^2/b$, w/ $\boxed{K_e \sim Z^{4/3} e^2/a_0}$.

(D) From part (A), the Coulomb interaction between a given electron and the nucleus is: $V_{ne} \sim Ze^2/r_e \sim Z^{\frac{4}{3}} e^2/a_0$, and part (B) ⇒ that electron has K.E. of size $K_e \sim Z^{\frac{4}{3}} e^2/a_0$.* So total $E_e \sim Z^{\frac{4}{3}} e^2/a_0$ for one electron in the atom. For Z electrons, the total ionization energy will be: $\boxed{I \sim ZE_e \sim Z^{7/3} e^2/a_0}$.†

(E) From part (C): $v_e \sim \sqrt{K_e/m} \sim Z^{\frac{2}{3}}(e^2/\hbar)$, w/ $\boxed{v_e \sim Z^{\frac{2}{3}} \alpha c}$, $\alpha = \frac{e^2}{\hbar c} \simeq \frac{1}{137}$.

(F) The average angular momentum for an electron is: $L_e \sim r_e \times m v_e$. So...

$$L_e \sim (Z^{-\frac{1}{3}} a_0) \times m \times Z^{\frac{2}{3}} \alpha c = Z^{\frac{1}{3}} \frac{\hbar^2}{me^2} \times m \times \frac{e^2}{\hbar}, \text{ w/ } \boxed{L_e \sim Z^{\frac{1}{3}} \hbar},$$

by using parts (A) & (E).

(G) In the Bohr theory, the radial quantum # n for a given electron shows up by quantizing its ∡ momentum L_e according to: $L_e = n\hbar$. Then, from part (F), we have immediately: $\boxed{n \sim Z^{1/3}}$.

---

† e-e repulsion, i.e. $\frac{1}{2}Z(Z-1)V_{ee}$, w/ V_{ee} in part (B), reduces I by ~ factor 2.

★ By the Virial Theorem (Davydov, p.57): $\langle K_e \rangle = \frac{1}{2}|\langle V_{ne}\rangle|$, for the Coulomb potential.