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Practice for Qualifying Exams

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Electron in a spherical well

An electron is in a spherical well of radius a and depth V_0, i.e., the non-relativistic Hamiltonian is

$$H = \frac{\vec{p}^{\,2}}{2m} + V \quad \textbf{(1)}$$

with m = the mass of an electron and

$$\begin{aligned} V &= -V_0 \quad r \le a \\ V &= 0 \quad r > a \end{aligned} \quad \textbf{(2)}$$

In this problem, we take $\frac{h}{2\pi} = 1$. The solutions of the Schrodinger equation are of the form $R(r)Y_{lm}(\theta,\phi)\chi_s$, where $R(r)$ is the radial wave equation, $Y_{lm}(\theta,\phi)$ is a spherical harmonic, and χ_s is a non-relativistic spinor. $R(r)$ is a solution to the equation

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{dR}{dr}\right] + \left[2m(E-V) - \frac{l(l+1)}{r^2}\right]R = 0 \quad \textbf{(3)}$$

where E is the energy of the state.

Note that in spherical coordinates, the ∇^2 operator has the form

$$\nabla^2 = \frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{dR}{dr}\right] + \frac{1}{r^2}\Omega(\theta,\phi) \quad \textbf{(4)}$$

where Ω is an operator in the angular variables. The differential equation satisfied by spherical Bessel or Hankel functions is

$$\frac{1}{x^2}\frac{d}{dx}\left[x^2\frac{dF_l(x)}{dx}\right] + \left[1 - \frac{l(l+1)}{x^2}\right]F_l(x) = 0 \quad \textbf{(5)}$$

(a) Explain what properties of the spherical harmonics are used to obtain equation (3) starting with the Hamiltonian given in equation (1). Note the form of the ∇^2 operator given above.

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V$$
$$H\psi = E\psi$$
$$\left[\nabla^2 + 2m(E - V)\right]\psi = 0$$

Next, separation of variables is assumed so that:

$$\left[\nabla^2 + 2m(E - V)\right]R(r)Y_{lm}(\theta,\phi) = 0$$

Now when one expands the ∇^2 operator, one gets

$$\left[\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{d}{dr}\right] + \frac{1}{r^2}\Omega(\theta,\phi) + 2m(E - V)\right]R(r)Y_{lm}(\theta,\phi) = 0$$

This is particularly convenient, since the spherical harmonics are orthogonal eigenfunctions of the spherical harmonic differential equation, here written $\Omega(\theta,\phi)$, with eigenvalue $-l(l+1)$. At this point, it is clear that by allowing the spherical harmonic differential equation to commute with the radial portion and act on the spherical harmonic, then dividing out the spherical harmonic portion will give (3) exactly.

(b) For our spherical well problem, what conditions must $R(r)$ satisfy at:

(i) $r = 0$

Since this wave function must be continuous in space, I see that it must without a doubt have a derivative of zero at the origin or otherwise the spherical harmonics approaching from either side could force a discontinuity as one approaches from either side:

$$R'(0) = 0 \quad if \quad l = 0$$
$$no \quad constraint \quad otherwise$$

Second, I see that a discontinuity could be imposed by the spherical harmonics if the spherical harmonic is not spherically symmetric:

$$R(0) = 0 \quad if \quad l \neq 0$$
$$R(0) \quad finite \quad otherwise$$

(ii) $r = a$

At this boundary, the wave function must be continuous:

$$R_{r>a}(a) = R_{r<a}(a) \quad and \quad R'_{r>a}(a) = R'_{r<a}(a)$$

(iii) $r \to \infty$

The wave function must be normalizable

$$R(\infty) = 0$$

(c) The solutions for $R(r)$ for bound electrons are spherical Bessel functions $j_l(\alpha r)$ inside the well and spherical Hankel functions $h_l(\beta r)$ outside the well. From the form of the differential equation for the spherical Bessel or Hankel functions given above, what are α and β in terms of the quantities given? The energies depend on the principal quantum number n as well as l. How is this reflected in the radial equations?

Obeying the Bessel functions inside the well, I have

$$\frac{1}{x^2}\frac{d}{dx}\left[x^2\frac{dR}{dx}\right] + \left[1 - \frac{l(l+1)}{x^2}\right]R = 0$$

$$has \quad solutions \quad h_l(x), j_l(x)$$

$$Define \quad x = Cr$$

$$\frac{d}{dx} = \frac{dr}{dx}\frac{d}{dr} = \frac{1}{C}\frac{d}{dr}$$

Substitute,

$$\frac{1}{C^2r^2}\frac{1}{C}\frac{d}{dr}\left[C^2r^2\frac{1}{C}\frac{dR}{dr}\right] + \left[1 - \frac{l(l+1)}{C^2r^2}\right]R = 0$$

$$\frac{1}{C^2r^2}\frac{d}{dr}\left[r^2\frac{dR}{dr}\right] + \left[1 - \frac{l(l+1)}{C^2r^2}\right]R = 0$$

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{dR}{dr}\right] + \left[C^2 - \frac{l(l+1)}{r^2}\right]R = 0$$

$$Identify \quad \beta = \sqrt{2mE} \quad \alpha = \sqrt{2m(E+V_0)}$$

The principal quantum number as well as the orbital angular momentum will be tied up in the energy $E_{n,l}$ of which both α and β are functions, as shown above.

(d) Write down the conditions from which you can find the energy eigenstates for bound states of the spherical well.

Valid solutions will be fixed by the boundary condition at the border of the sphere:

$$Ah_l\left(\sqrt{2mE_{n,l}}\,a\right) = Bj_l\left(\sqrt{2m\left(E_{n,l}+V_0\right)}a\right)$$
$$Ah_l'\left(\sqrt{2mE_{n,l}}\,a\right) = Bj_l'\left(\sqrt{2m\left(E_{n,l}+V_0\right)}a\right)$$
$$\int_{all\ \ space} \left|\psi\left(\vec{r}\right)\right|^2 = 1$$

Many energies E may be possible for a given l, corresponding to the radial portion.

(e) Two electrons are placed in the well. Neglecting interactions and assuming that the electrons are distinguishable, write down the wave functions of the two-particle system. Your solutions should correspond to total orbital and total spin quantum numbers.

These will be given by Clebsch-Gordan coefficients. I have:

$$S \in \{0,1\}$$

$$v = valid \quad wavefunction \quad count$$
$$\psi_{L,S}\left(\vec{x}_1,\vec{x}_2\right) = \frac{1}{\sqrt{v}}\left[\sum_{n=0}^{\infty}\sum_{m=0}^{\infty} R_n\left(r_1\right)R_m\left(r_2\right)\right]$$
$$\cdot\left[\sum_{i=0}^{\infty}\sum_{j=\max(i-L,0)}^{i+L}\sum_{k=-i}^{i}\sum_{M_L=-L}^{L}\left\langle i \quad k \quad ; \quad j \quad M_L-k \middle| L \quad M_L\right\rangle \psi_{i,k}\left(\theta_1,\phi_1\right)\psi_{j,M_L-k}\left(\theta_2,\phi_2\right)\right]$$
$$\cdot\left[\sum_{f=\left\{-\frac{1}{2},\frac{1}{2}\right\}}\sum_{M_S=-S}^{S}\left\langle \frac{1}{2} \quad f \quad ; \quad \frac{1}{2} \quad M_S-f \middle| S \quad M_S\right\rangle \chi_f\left(\vec{x}_1\right)\chi_{M_S-f}\left(\vec{x}_2\right)\right]$$
$$\cdot\left[1-\delta_i^j\delta_k^{M_L-k}\delta_n^m\delta_f^{M_S-f}\right]$$

Note that I also have removed the case where the particles had the same wave function.

(f) There is a spin-spin interaction between the two electrons, which has the approximate form $g_S\left(\vec{S}_1\cdot\vec{S}_2\right)$. Show how this interaction arises from the classical interaction between two magnetic dipoles and express g_S in terms of the properties of the electron. Do not attempt a detailed derivation, but give a qualitative explanation of the origin of the spin-spin force.

Suppose two electrons were overlap one another but interact only via their magnetic moments (think of their spins as current loops). There would be a torque on one from the field on the other, and vice-versa.

$$\mu_B : Bohr \quad Magneton = \frac{e\hbar}{2m}$$

I then have: $E = -\vec{\mu}_B \cdot \vec{B}_{other \quad spin}$ and similarly,

$$\vec{\mu} = \frac{-e}{m_e}\vec{S}_e$$

For a magnetic dipole,

$$\vec{B} = \frac{\mu_0}{4\pi r^3}\left[3(\vec{\mu}\cdot\hat{r})\hat{r} - \vec{\mu}\right] - \frac{2\mu_0}{3}\vec{\mu}\delta(\vec{r})$$

Then,

$$E = -\vec{\mu}_B \cdot \left[\frac{\mu_0}{4\pi r^3}\left[3(\vec{\mu}\cdot\hat{r})\hat{r} - \vec{\mu}\right] - \frac{2\mu_0}{3}\vec{\mu}\delta(\vec{r})\right]$$

$$= -\frac{\mu_0}{4\pi r^3}\left[3(\vec{\mu}_{B1}\cdot\hat{r})(\vec{\mu}_{B2}\cdot\hat{r}) - \vec{\mu}_{B1}\cdot\vec{\mu}_{B2}\right] - \frac{2\mu_0}{3}(\vec{\mu}_{B1}\cdot\vec{\mu}_{B2})\delta(\vec{r})$$

$$= -\frac{\mu_0}{4\pi r^3}\left[3\frac{e^2}{m_e^2}(\vec{S}_1\cdot\hat{r})(\vec{S}_2\cdot\hat{r}) - \vec{S}_1\cdot\vec{S}_2\right] - \frac{2\mu_0}{3}\frac{e^2}{m_e^2}\vec{S}_1\cdot\vec{S}_2\delta(\vec{r})$$

Taking only the portions depending only on $\vec{S}_1\cdot\vec{S}_2$,

$$g_S = \left[\frac{\mu_0}{4\pi r^3}\frac{e^2}{m_e^2} - \frac{2\mu_0}{3}\frac{e^2}{m_e^2}\delta(\vec{r})\right]\vec{S}_1\cdot\vec{S}_2$$

(g) Treating the interaction of part (f) as a small perturbation, estimate the change in the energies of the lowest-energy states you listed in part (e).

$\int_{all \quad space} g_S \psi^* \psi dV$ will give an estimate. Recall that

$$(\vec{S}_1 + \vec{S}_2)^2 = \vec{S}_1^2 + \vec{S}_2^2 + 2\vec{S}_1\cdot\vec{S}_2$$

$$\vec{S}_1\cdot\vec{S}_2 = \frac{(\vec{S}_1 + \vec{S}_2)^2 - \vec{S}_1^2 - \vec{S}_2^2}{2}$$

so that only the total spin and individual spins take part. There is then shifting but no splitting in the states above.

$$\vec{S}_1\cdot\vec{S}_2 = \frac{(\vec{S}_1 + \vec{S}_2)^2 - \vec{S}_1^2 - \vec{S}_2^2}{2} = -\frac{3}{4}\hbar^2(if \quad S = 0) \quad \frac{1}{4}\hbar^2(if \quad S = 1)$$

and the integration is something like

$$\Delta E = \vec{S}_1 \cdot \vec{S}_2 \cdot 4\pi \cdot \int_0^\infty R_n^2(r)\left[\frac{\mu_0}{4\pi r^3}\frac{e^2}{m_e^2} - \frac{2\mu_0}{3}\frac{e^2}{m_e^2}\delta(r)\right] r^2 dr$$

which is on the order of

$$\Delta E = \left[\vec{S}_1 \cdot \vec{S}_2\right]_{given \quad above} \cdot 4\pi \cdot \frac{\mu_0 e^2}{m_e^2}\left[\int_0^\infty R_n^2(r)\left[\frac{1}{4\pi r^3} - \frac{2}{3}\delta(r)\right] r^2 dr \approx 1\right]$$

(h) The electrons are identical fermions. How are the wave functions of part (e) modified? Prove that if two electrons are placed in the same l-orbit, solutions with total spin S = 1 (triplet states) vanish. Give a qualitative explanation in terms of the Pauli Exclusion Principle.

The states in part (e) are anti-symmetrized if the electrons are considered identical. This means that similar states will be combined so that the exchange of particle numbers gives an overall -1 factor.

In the case of identical l-orbit, then, I see from part (e) that all portions of the wave functions match under exchange except the spin part:

$$\left[\sum_{f=\left\{-\frac{1}{2},\frac{1}{2}\right\}} \sum_{M_S=-S}^{S} \left\langle \frac{1}{2} \quad f \quad ; \quad \frac{1}{2} \quad M_S - f \middle| S \quad M_S \right\rangle \left(\chi_f(\vec{x}_1)\chi_{M_S-f}(\vec{x}_2)\right)\right]$$

In an antisymmetric combination, when I switch the two particles to combine I need an overall negative factor. In the possibilities $\left\langle \frac{1}{2} \quad \left\{\pm\frac{1}{2}\right\} \quad ; \quad \frac{1}{2} \quad \left\{\pm\frac{1}{2}\right\} \middle| \{0,1\} \quad \{0,1\} \right\rangle$, the only qualifying coefficient pair that is nonzero and brings a negative factor in swapping is is $\left\langle \frac{1}{2} \quad \frac{1}{2} \quad ; \quad \frac{1}{2} \quad -\frac{1}{2} \middle| 0 \quad 0 \right\rangle = -\left\langle \frac{1}{2} \quad -\frac{1}{2} \quad ; \quad \frac{1}{2} \quad \frac{1}{2} \middle| 0 \quad 0 \right\rangle$.

In terms of the Pauli exclusion principle, one can think of a electrons in the same radial and angular momentum orbital. This orbital must be occupied by one “spin-up” and one “spin-down” electron.

(i) The system is put in a heat bath at temperature T. If an electron is put in the well and comes to thermal equilibrium, what is the ratio of probabilities that the electron is in the first excited versus the ground state of the system? Assume that the quantum energy levels are not changed by the heat bath.

Using the Canonical Ensemble in a two-state system, I can assume that this ratio is roughly

$$\frac{e^{-\frac{1}{kT}\varepsilon_1}}{e^{-\frac{1}{kT}\varepsilon_0}}$$

I will assume that for the one-electron system, the lowest energy states are both for the lowest radial state and for different total angular momentum states, 0 and 1. The form of the momentum operator then gives

$$\left[\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{d}{dr}\right]+\frac{1}{r^2}\Omega(\theta,\phi)+2m(E-V)\right]R_1(r)Y_{00}(\theta,\phi)=0$$

$$\left[\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{d}{dr}\right]+2m(E_0-V)\right]R_1(r)=0$$

and

$$\left[\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{d}{dr}\right]+\frac{1}{r^2}\Omega(\theta,\phi)+2m(E-V)\right]R_1(r)Y_{10}(\theta,\phi)=0$$

$$\left[\frac{1}{r^2}\left(\frac{d}{dr}\left[r^2\frac{d}{dr}\right]-2\right)+2m(E_1-V)\right]R_1(r)=0$$

$$\left[\frac{1}{r^2}\left(\frac{d}{dr}\left[r^2\frac{d}{dr}\right]-2\right)+2m(E_1-V)\right]R_1(r)=\left[\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{d}{dr}\right]+2m(E_0-V)\right]R_1(r)$$

$$\left[-\frac{2}{r^2}+2m(E_1-V)\right]R_1(r)=[2m(E_0-V)]R_1(r)$$

This integration to collapse the radius, however, is nontrivial—at least I get an order of magnitude from the additional term:

$$\int_0^a\left[-\frac{2}{r^2}+2m(E_1-V)\right]R_1(r)dr=\int_0^a[2m(E_0-V)]R_1(r)dr$$

$$\approx -2\ln(a)+2m(E_1-V)=2m(E_0-V)$$

$$E_1=E_0+\ln a\frac{\hbar^2}{m}$$

where time-averaging over states assumed stationary will remove the seconds from the h-bar units.

$$\frac{e^{-\frac{1}{kT}\varepsilon_1}}{e^{-\frac{1}{kT}\varepsilon_0}}=e^{-\frac{\hbar^2}{kTm_e}\ln a}$$

(j) You were not given the value of T in part (i). Describe an experiment that would enable you to measure the temperature of the system. Briefly discuss

the possible errors and the design of your experiment to achieve the measurement. Assume that a is atomic size and V_0 has the scale of electron-volts.

First, notice that the transition from the zero angular-momentum to one angular-momentum state here could plausibly come from excitation or emission of a circularly-polarized photon.

Assume that the heat-transfer efficiency is perfect between the object and the heat bath. Using this probability, I see that no transition would occur from a photon incident on the well if the particle were already in an excited state and that absorption and re-emission would occur if the particle were in the ground state.

In this case, then, I fire a fine beam of photons of the desired energy into the object, and then observe the proportion that is allowed to pass through. The temperature can then be deduced from part (i) since the proportion of photons that passes through is equal to the proportion of measurements that found the electron in the first excited-state.