Quantum Mechanics: Problems 3

1. Consider the coupling of two angular momenta $\mathbf{J}_1$ and $\mathbf{J}_2$ (which may be either orbital or spin angular momenta) to give a resultant $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$. (This coupling might be brought about, for example, by the spin-orbit interaction considered in the following question, where $\mathbf{J}_1 = \mathbf{L}$, $\mathbf{J}_2 = \mathbf{S}$, and the interaction which couples these two sources of angular momentum together to give a resultant $\mathbf{J} = \mathbf{L} + \mathbf{S}$ is the spin-orbit coupling Hamiltonian $H_{\mathrm{so}} = \zeta\, \mathbf{L} \cdot \mathbf{S}$.)

The operator for the square of the total angular momentum is

$$J^2 = (\mathbf{J}_1 + \mathbf{J}_2)^2 = J_1^2 + J_2^2 + 2\mathbf{J}_1 \cdot \mathbf{J}_2 = J_1^2 + J_2^2 + 2\left(J_{1x}J_{2x} + J_{1y}J_{2y} + J_{1z}J_{2z}\right)$$

and the operator for the projection of the total angular momentum on the z axis is

$$J_z = J_{1z} + J_{2z}$$

where the operators J_{ix}, J_{iy} and J_{iz} satisfy the usual commutation relations

$$\left[J_i^2, J_{ix}\right] = \left[J_i^2, J_{iy}\right] = \left[J_i^2, J_{iz}\right] = 0,$$

$$\left[J_{ix}, J_{iy}\right] = i\hbar\, J_{iz}, \quad \left[J_{iy}, J_{iz}\right] = i\hbar\, J_{ix}, \quad \left[J_{iz}, J_{ix}\right] = i\hbar\, J_{iy},$$

for $i = 1$ and 2. Note also that each component of $\mathbf{J}_1$ commutes with each component of $\mathbf{J}_2$ because the two operators operate on different degrees of freedom.

(a) Use the basic angular momentum commutation relations to verify that

$$\left[J^2, J_1^2\right] = \left[J^2, J_2^2\right] = 0$$

and

$$\left[J_z, J_1^2\right] = \left[J_z, J_2^2\right] = 0,$$

and hence that it is possible to specify all four of the observables corresponding to J_1^2, J_2^2, J^2 and J_z simultaneously and precisely.

(b) Go on to show that

$$\left[J^2, J_{1z}\right] \neq 0 \quad \text{and} \quad \left[J^2, J_{2z}\right] \neq 0,$$

and hence that the projections of the individual angular momenta $\mathbf{J}_1$ and $\mathbf{J}_2$ on the z axis cannot be specified at the same time as the square of the total angular momentum $\mathbf{J}$.

2. Several different electronic states can arise from an atomic electron configuration $(n\ell)^k$ where k is less than the number required for a closed shell. Electrostatic interactions between the open shell electrons cause moderately large energy splittings between these states, which are labelled by orbital and spin angular momentum quantum numbers L and S and which are referred to as *terms*. Within each term, smaller splittings occur due to spin-orbit coupling (a magnetic interaction between the spin magnetic moment and the magnetic field generated by the motion of charged particles about the electron in question). These splittings are referred to as fine structure and result in individual *levels* labelled by the total electronic angular momentum quantum number J. Assuming that L, S and J are all "good" quantum numbers, which is a reasonable approximation for light atoms, each atomic energy level E_{LSJ} is given by

$$E_{LSJ} = E_{LS} + \langle LSJ \,|\, H_{\mathrm{so}} \,|\, LSJ \rangle$$

where E_{LS} is the term energy, $H_{\mathrm{so}} = \zeta\,\mathbf{L}\cdot\mathbf{S}$ is the spin-orbit interaction Hamiltonian and ζ is the spin-orbit coupling constant of the atom.

(a) Use the fact that the total electronic angular momentum operator $\mathbf{J}$ is given by the vector sum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ to express H_{so} in terms of the operators L^2, S^2 and J^2, and hence obtain an expression for E_{LSJ} in terms of the quantum numbers L, S and J.

(b) An analysis of the electronic spectrum of a certain atom shows that the ground term is split into three levels with relative energies of 0, 14 and 42 cm^{-1}. Use your expression for E_{LSJ} from part (a) to assign J values to the three levels and obtain a value for ζ. What are the possible values of L and S for this term?

3. A quartic oscillator has a potential proportional to the fourth power of the displacement from equilibrium so that the Hamiltonian is

$$H = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^4.$$

Find the best variational value of the parameter α in the trial function

$$\psi(x) = e^{-\frac{1}{2}\alpha x^2}$$

and determine the corresponding energy. How might this approximate wavefunction be improved?

$$\textit{Note}: \quad \int_{-\infty}^{\infty} x^{2n} e^{-ax^2}\, dx = \frac{1.3.5\ldots(2n-1)}{(2a)^n}\sqrt{\frac{\pi}{a}}.$$

4. Suppose that an approximate wavefunction for a system can be written in the form $\psi = c_1\phi_1 + c_2\phi_2$ where ϕ_1 and ϕ_2 are certain real orthonormal functions and c_1 and c_2 are real constants.

(a) Write down the expectation value $E = \langle H \rangle$ of the energy in terms of the integrals

$$\alpha_1 = \langle \phi_1 \,|\, H \,|\, \phi_1 \rangle,$$

$$\alpha_2 = \langle \phi_2 \,|\, H \,|\, \phi_2 \rangle,$$

and

$$\beta = \langle \phi_1 \,|\, H \,|\, \phi_2 \rangle = \langle \phi_2 \,|\, H \,|\, \phi_1 \rangle.$$

(b) According to the variational principle, the best wavefunction ψ is found by choosing c_1 and c_2 so as to minimize E. Show that this happens when c_1 and c_2 satisfy the *secular equations*

$$(\alpha_1 - E)\, c_1 + \beta\, c_2 = 0,$$
$$\beta\, c_1 + (\alpha_2 - E)\, c_2 = 0.$$

(c) These equations have a non-zero solution for the coefficients c_1 and c_2 if and only if the secular determinant vanishes:

$$\begin{vmatrix} \alpha_1 - E & \beta \\ \beta & \alpha_2 - E \end{vmatrix} = 0.$$

Show that the energies satisfying this equation are

$$E_{\pm} = \frac{1}{2}(\alpha_1 + \alpha_2) \pm \frac{1}{2}\left[(\alpha_1 - \alpha_2)^2 + 4\beta^2 \right]^{\frac{1}{2}}.$$

(d) Use the secular equations to find the values of the coefficients c_1 and c_2 corresponding to each of these two energies in the special case where $\alpha_1 = \alpha_2$ and $\beta < 0$. (This case is relevant to both the σ molecular orbitals of H_2 and the π molecular orbitals of ethylene – see your Valence lectures in the Trinity term.)

5. This final question introduces you to a typical barrier tunnelling problem. Consider the one-dimensional motion of a particle of mass m and energy E on the x axis subject to the potential $V(x)$ given by

$$V(x) = \begin{cases} \infty, & x < 0, \\ 0, & 0 < x < a, \\ V_0, & a < x < b, \\ 0, & x > b, \end{cases}$$

where V_0 is a constant greater than E.

(a) Sketch the potential.

(b) Show that a wavefunction of the form

$$\psi(x) = \begin{cases} 0, & x \leq 0, \\ \sin(kx), & 0 \leq x \leq a, \\ A\exp(k'x) + B\exp(-k'x), & a \leq x \leq b, \\ C\sin(kx) + D\cos(kx), & x \geq b, \end{cases}$$

satisfies the Schrödinger equation. What is the physical significance of k?

(c) Give, and explain, the conditions which determine the constants A, B, C, D. (*Hint:* You clearly have to find 4 equations relating these 4 unknowns, but once you have found these 4 equations you are *not* required to go ahead and actually solve them for A, B, C and D.)

(d) Show that if $b \to \infty$ the allowed values of the energy satisfy

$$\cot\left(\frac{2mEa^2}{\hbar^2}\right)^{\frac{1}{2}} = -\left(\frac{V_0 - E}{E}\right)^{\frac{1}{2}}.$$

(e) If E is a root of this equation, but b is finite, the boundary condition at $x = 0$ and the continuity condition at $x = a$ require that the wavefunction is unchanged in the region $x \leq b$. Show that in this case the "transmission coefficient" $\psi(b)^2/\psi(a)^2$ is $\exp[-2k'(b-a)]$ and therefore decreases exponentially when either the barrier height or the barrier width is increased.