16.3 Problem Set III

1. Atomic structure: The following question begins with a recapitulation of the leading relativistic corrections to the Schrödinger Hamiltonian of hydrogen-like atoms.

   Explain the physical origin of the following terms in the Hamiltonian for one-electron atoms:

   $$\begin{aligned} \hat{H}_1 &= -\frac{(\hat{\mathbf{p}}^2)^2}{8m^3c^2} \\ \hat{H}_2 &= \frac{1}{2m^2c^2}\frac{(\partial_r V)}{r}\,\hat{\mathbf{L}}\cdot\hat{\mathbf{S}} \\ \hat{H}_3 &= \frac{Ze^2}{4\pi\epsilon_0}\frac{\hbar^2}{8(mc)^2}4\pi\delta^{(3)}(\mathbf{r})\,. \end{aligned}$$

   Here m denotes the electron mass, V the electrostatic potential generated by the nucleus, and Z the atomic number.

   The hydrogenic radial wavefunctions have the form,

   Explicit evaluation of numerical factors is **not** required.

   $$\psi_{n\ell}(r) = \left(\frac{Z}{a_0}\right)^{3/2} G_{n\ell}\left(\frac{Zr}{a_0}\right)\exp\left[-\frac{Zr}{na_0}\right],$$

   where a_0 denotes the Bohr radius and $G_{n\ell}$ is a polynomial function of its argument. Show that the expectation values of the energies associated with the three terms listed above all have the same dependence on Z. (Part IB Advanced Physics 1993.)

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2. Atomic structure: The following problem addresses the electron configuration of multi-electron atoms. In completing this question, you should remind yourself of the physical origin of the Hund's rules.

   Determine the possible spectroscopic terms, ${}^{2S+1}L_J$, for each of the following electron configurations: $(2s)(3p)$, $(2p)^2$, $(3d)^2$, $(3d)^{10}$, and $(3d)^9$.

   Using Hund's rules, determine the angular momentum quantum numbers of the ground state of Sm, which has electron configuration $(4f)^6$.

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3. Atomic structure: The following problem addresses the interplay between LS and jj coupling.

   The ground state of Ge has the configuration $(4p)^2$ and spectroscopic term ${}^3P_0$. Explain the meaning of this notation and state the assumptions about atomic structure on which it is based.

   Derive the allowed states of a $(3p)^1(4s)^1$ configuration in (i) LS coupling and (ii) jj coupling, sketching an energy level diagram in each case. Explain the interactions which give rise to the various energy splittings.

   For a certain element, the energy levels given right, which are specified relative to the ground state, are known to belong to a $(6p)^1(7s)^1$ configuration. Deduce what you can about the quantum numbers appropriate to each energy level, given their relative magnitude and the fact that only levels (b) and (d) decay to the $J = 0$ ground state by electric dipole transitions.

   (a) 4.334 eV
   (b) 4.375 eV
   (c) 5.975 eV
   (d) 6.130 eV

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4. †Atomic spectra: By drawing upon your knowledge about the properties of multielectron atoms, the following problem requires the decipher of the atomic spectra of sodium.

   The three groups of lines shown right, whose frequencies are given in units of 10^{15} Hz, are observed in the emission spectrum of atomic sodium. By identifying the spectral lines with specific states of sodium, make an index of the associated transitions. In doing so, you will find it helpful to address the following questions: (i) What are the appropriate quantum numbers for the ground state and low energy excited states of sodium? (ii) Which energy levels are split by the spin-orbit interaction? (iii) How (qualitatively) does the spin-orbit coupling depend on n? (iv) Which transitions are allowed by the dipole selection rules?

   I Doublets with decreasing doublet splitting:

   0.50899 0.90782 1.05086 1.11848
   0.50847 0.90765 1.05079 1.11845

   II Doublets with constant doublet splitting:

   0.26340 0.48713 0.58225 0.63142
   0.26288 0.48662 0.58174 0.63090

   III Triplets, with two lines sometimes unresolved:

   0.36635 0.52756 0.60207 0.64267
   0.36583_3 0.52704 0.60165 0.64215
   0.36583_1

   Draw an energy level diagram, taking the $(3s)$ state as the zero of energy, and answer the following questions:

   (a) What is the energy difference between the $(5p)$ $J = 3/2$ and $J = 1/2$ states in sodium?

   (b) Estimate the first ionization energy of sodium.

   (c) What are the relative importances of the ℓ-dependence of the electron-electron energy, and the j-dependence of the spin-orbit energy in the $n = 3$ and $n = 6$ shells?

5. Zeeman effect: This problem involves the study of the infleunce of a weak magnetic field on the spectrum of a multielectron atom. Here we are interested in exploring the interplay between LS coupling and the influence of the external field.

   For an atom characterised by LS coupling, and subject to a weak uniform magnetic field, derive the expression for the Landé g-factor,

$$g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} .$$

   In a Zeeman experiment, the ${}^3\mathrm{S}_1 \rightarrow {}^3\mathrm{P}_1$ emission of an ensemble of such atoms is observed in the presence of a weak magnetic field B. Describe the resulting Zeeman structure of the atomic levels, and indicate which transitions amongst the split levels are allowed in an electric dipole transition. Sketch the form of the line spectrum seen in some general direction before and after the field is applied. Label, in units of $\mu_\mathrm{B} B$ where μ_B is the Bohr magneton, the positions of the components relative to the energy of the unperturbed transition.

   Hint: Consider how the electric field couples to the electric dipole and how this translates to constraints on the allowed change in M_J.

   If the emission is viewed perpendicular to the direction of the magnetic field, how many lines will be observed and what polarization states will they have?

6. Atomic structure: As well as the interaction between the spin and orbital degrees of freedom of the electron which follow from the relativistic corrections, the magnetic field generated by the nuclear magnetic momentum also lead to corrections to the electron Hamiltonian. These corrections are known as hyperfine coupling. The following problem involves exploring the

evolution of the hyperfine spectrum of the hydrogen atom in the presence of a weak magnetic field.

The magnetic part of the Hamiltonian for a hydrogen atom in the $1s$ state, in the presence of a constant magnetic field B along the z axis, may be cast in the form

$$\hat{H} = B\left(\mu_{\rm e}\sigma_z^{(\rm e)} + \mu_{\rm p}\sigma_z^{(\rm p)}\right) + W\boldsymbol{\sigma}^{(\rm e)}\cdot\boldsymbol{\sigma}^{(\rm p)}\,,$$

where the superscripts e and p refer to the electron and proton, the vector components of $\boldsymbol{\sigma}$ are the Pauli spin operators, $\mu_{\rm e,p}$ are the respective magnetic dipole moments, and W is a constant.

(i) Explain the physical origin of each term in the Hamiltonian.

(ii) Using as a basis the states $|\uparrow_{\rm e}\rangle\otimes|\uparrow_{\rm p}\rangle$, $|\uparrow_{\rm e}\rangle\otimes|\downarrow_{\rm p}\rangle$, $|\downarrow_{\rm e}\rangle\otimes|\uparrow_{\rm p}\rangle$, $|\downarrow_{\rm e}\rangle\otimes|\downarrow_{\rm p}\rangle$, and neglecting the small term in $\mu_{\rm p}$, show that the $\hat{H}$ may be represented by the matrix

$$\begin{pmatrix} b+W & 0 & 0 & 0 \\ 0 & b-W & 2W & 0 \\ 0 & 2W & -b-W & 0 \\ 0 & 0 & 0 & -b+W \end{pmatrix},$$

where $b = \mu_B B$. (Explain why $\mu_{\rm p}$ is small in comparison to $\mu_{\rm e}$.)

(iii) Determine the energy levels and sketch their evolution as a function of B, labelling them with as much information as possible about the total angular momenta of the states.

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7. Molecular structure: This problem concerns the application of the LCAO method to molecular bonding in the H_3^+ ion.

Explain what is meant by the Born-Oppenheimer approximation and discuss how molecular wavefunctions can be formed within this approximation by using the Linear Combination of Atomic Orbitals (LCAO).

The H_3^+ ion exists as an isosceles triangle (distance $d_{12} = d_{23} \neq d_{31}$), with the internal bond angle $60° \le \theta \le 180°$. Treating this ion in the LCAO approximation, introducing the $1s$ basis state wavefunctions, $|\psi_i\rangle$ for the $i^{\rm th}$ atom, show that the electron energy levels are solutions of the secular equation

$$\begin{vmatrix} \alpha-E & \beta & \gamma\beta \\ \beta & \alpha-E & \beta \\ \gamma\beta & \beta & \alpha-E \end{vmatrix} = 0\,,$$

where $\alpha = \langle\psi_1|\hat{H}|\psi_1\rangle = \langle\psi_2|\hat{H}|\psi_2\rangle = \langle\psi_3|\hat{H}|\psi_3\rangle$, $\beta = \langle\psi_1|\hat{H}|\psi_2\rangle = \langle\psi_2|\hat{H}|\psi_3\rangle$, and $\beta\gamma = \langle\psi_1|\hat{H}|\psi_3\rangle$, where $\hat{H}$ is the Hamiltonian for the ion. In this case, as an approximation, you may ignore the overlap integrals, $\langle\psi_i|\psi_j\rangle$. Find the energy levels and sketch them in the range $0 \le \gamma \le 1$. Show that the ground state must be a spin singlet, and predict which value of γ should be most stable. Qualitatively, how would you expect γ to vary with θ, and hence, what would you expect to be the value of θ in the most stable configuration? [Note that the matrix element β is negative.] (Part II 1998)

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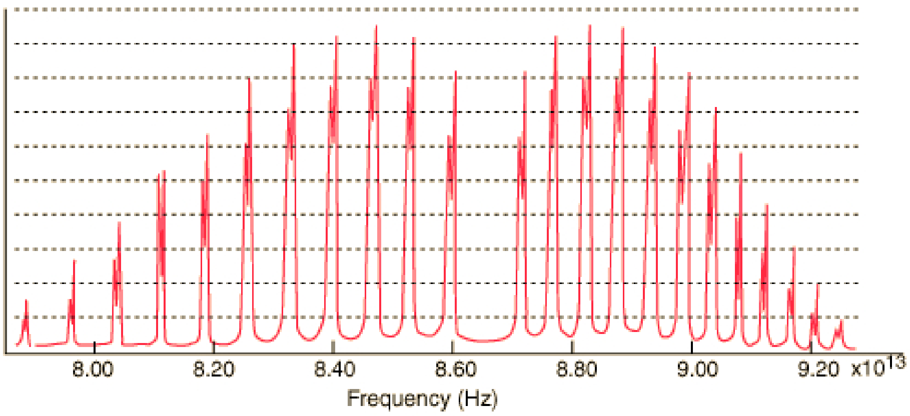

Figure 16.1: Infra-red rotation-vibration band spectrum of HCl measured in Hz.

8. Molecular structure: This problem explores the relative influence of valance bonding in H_2.

   In the pure valence bonding approximation, the electronic ground state wavefunction of the H_2 molecule is given by

   $$\psi^{\mathrm{VB}} = C[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)]\,,$$

   where ψ_a and ψ_b are the (real) ground state wavefunctions of the two hydrogen atoms.

   (i) Express the normalization constant C in terms of the overlap integral $S = \int d^3r\, \psi_a\psi_b$.

   (ii) Express ψ^{VB} in terms of the molecular bonding and antibonding orbitals, $(\sigma_g(1), \sigma_g(2))$ and $(\sigma_u^*(1), \sigma_u^*(2))$, defined in lectures.

   (iii) Hence find a second molecular state $\psi_\perp$ orthogonal to ψ^{VB} and interpret it in terms of covalent and ionic components.

   (iv) Use the result $S = (1 + \rho + \rho^2/3)e^{-\rho}$ with $\rho = R/a_0 \simeq 1.6$ to estimate the configuration mixing (i.e. the relative contributions of the VB and ionic bond) in H_2.

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9. Molecular spectra: This question addresses the features of the rotation-vibration spectra of the diatomic molecule HCl. It also provides an exercise in the application of selection rules to radiative transitions.

   Explain the following features of the rotation-vibration absorption spectrum of HCl shown in Fig. 16.1: (i) the missing peak at the centre, (ii) the double peak structure, (iii) the line spacing and why it is uneven, (iv) the intensity as a function of wave number. Determine the values of as many molecular parameters as you can from the spectrum.

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