

Problems Chapter 9

Quantum Mechanics

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Problem 1

An harmonic oscillator with mass m and frequency ω is subjected to an external perturbation. Compute the first and second order corrections in perturbation theory to energy eigenvalues due to the following perturbations:

$$V = : g_1 q; \frac{1}{2} g_2 q^2; \frac{1}{2} g_3 q^3; \frac{1}{2} g_4 q^4.$$

● Solution

■ Hamiltonian and operators

The unperturbed Hamiltonian is

$$H_0 = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 q^2.$$

Matrix elements for perturbations can be computed or performing integrals with Hermite polynomials or using the decomposition in annihilation and creation operators:

$$q = \sqrt{\frac{\hbar}{2m\omega}} (a + a^\dagger); \quad p = -i \sqrt{\frac{m\omega\hbar}{2}} (a - a^\dagger); \quad H_0 = \hbar\omega \left(a^\dagger a + \frac{1}{2} \right). \quad (1.1)$$

Using $\text{ket}[n]$ for the state $|n\rangle$

$$a^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle; \quad a |n\rangle = \sqrt{n} |n-1\rangle; \quad (1.2)$$

and the decomposition (1) it is easy to show that

$$\begin{aligned} q |n\rangle &= \left(\frac{\hbar}{2m\omega} \right)^{1/2} \left(\sqrt{n+1} |n+1\rangle + \sqrt{n} |n-1\rangle \right) \\ q^2 |n\rangle &= \left(\frac{\hbar}{2m\omega} \right) \left(\sqrt{(n+1)(n+2)} |n+2\rangle + (2n+1) |n\rangle + \sqrt{n(n-1)} |n-2\rangle \right) \\ q^3 |n\rangle &= \left(\frac{\hbar}{2m\omega} \right)^{3/2} \\ &\quad \left(\sqrt{(n+1)(n+2)(n+3)} |n+3\rangle + 3(n+1)^{3/2} |n+1\rangle + 3n^{3/2} |n-1\rangle + \sqrt{n(n-1)(n-2)} |n-3\rangle \right) \\ q^4 |n\rangle &= \left(\frac{\hbar}{2m\omega} \right)^2 \left(\sqrt{(n+1)(n+2)(n+3)(n+4)} |n+4\rangle + (4n+6) \sqrt{(n+1)(n+2)} |n+2\rangle + \right. \\ &\quad \left. (6n^2 + 6n + 3) |n\rangle + (4n-2) \sqrt{n(n-1)} |n-2\rangle + \sqrt{n(n-1)(n-2)(n-3)} |n-4\rangle \right) \end{aligned}$$

Interactions q^2 and q^4 produce a first order effect on levels. This effect can be read from diagonal matrix elements of these operators

$$\begin{aligned} \Delta E_n &= \frac{1}{2} g_2 \langle n | q^2 | n \rangle = g_2 \left(\frac{\hbar}{2m\omega} \right) \left(n + \frac{1}{2} \right); \\ \Delta E_n &= \frac{1}{2} g_4 \langle n | q^4 | n \rangle = g_4 \frac{3}{2} \left(\frac{\hbar}{2m\omega} \right)^2 (1 + 2n + 2n^2). \end{aligned}$$

Operators q and q^3 produce a shift at second order. The first order contribution is zero by parity conservation and this is confirmed from absence of diagonal elements in their matrix elements. At second order the shift in energy levels is

$$\Delta E_n^{(2)} = \sum_{s \neq n} \langle \psi_0 | V | s \rangle \frac{1}{E_0 - E_s} \langle s | V | \psi_0 \rangle.$$

Only a finite number of intermediate states contribute to the sum.

□ **Operator q**

$$\Delta E_n^{(2)} = g_1^2 \left(\frac{|\langle n | q | n-1 \rangle|^2}{E_n - E_{n-1}} + \frac{|\langle n | q | n+1 \rangle|^2}{E_n - E_{n+1}} \right) = -\frac{1}{2} \frac{g_1^2}{m \omega^2}.$$

This result is obvious, a linear term in q can be reabsorbed by a translation of the quadratic potential:

$$\frac{1}{2} m \omega^2 q^2 + g_1 q = \frac{1}{2} m \omega^2 \left(q + \frac{g_1}{m \omega^2} \right)^2 - \frac{1}{2} \frac{g_1^2}{m \omega^2}.$$

□ **Operator q^3**

The only contributions different from zero are

$$\begin{aligned} \Delta E_n^{(2)} &= \frac{1}{4} g_3^2 \left(\frac{|\langle n | q^3 | n-1 \rangle|^2}{E_n - E_{n-1}} + \frac{|\langle n | q^3 | n+1 \rangle|^2}{E_n - E_{n+1}} + \frac{|\langle n | q^3 | n-3 \rangle|^2}{E_n - E_{n-3}} + \frac{|\langle n | q^3 | n+3 \rangle|^2}{E_n - E_{n+3}} \right) = \\ &= -\frac{g_3^2}{4 \hbar \omega} \left(\frac{\hbar}{2 m \omega} \right)^3 (30 n^2 + 30 n + 11). \end{aligned}$$

□ **Operator q^4**

The only contributions different from zero come from transitions to intermediate states $n, n \pm 2, n \pm 4$. A computation similar to the one above gives, for second order contribution:

$$\Delta E_n^{(2)} = -\frac{g_4^2}{4 \hbar \omega} \left(\frac{\hbar}{2 m \omega} \right)^4 (68 n^3 + 102 n^2 + 118 n + 42).$$

Problem 2

Let us consider the proton as a small homogeneous charged sphere of radius R . Compute how the hydrogen levels are affected by this hypothesis.

• Solution

□ **Hamiltonian**

Inside an homogeneous sphere of radius R and charge e the electrostatic potential is

$$V_{\text{sph}}[r] = e \left(\frac{3}{2R} - \frac{1}{2} \frac{r^2}{R^3} \right),$$

while outside is identical to usual Coulomb potential V_C . The difference between the two potentials can be considered as a small perturbation to e/r potential

$$H_I[r] = -e \left(V_{\text{sph}} - \frac{e}{r} \right) = -e^2 \left(\frac{3}{2R} - \frac{1}{2} \frac{r^2}{R^3} - \frac{1}{r} \right); \quad r \leq R. \quad (2.1)$$

The perturbation is radial, so energy corrections are computed by

$$\Delta E_{nL} = \int_0^R H_I[r] R_{nL}[r]^2 r^2 dr. \quad (2.2)$$

Using radial wave functions (a_B is the Bohr radius)

$$R_{1s}[r] = \frac{2}{a_B^{3/2}} e^{-\frac{r}{a_B}}; \quad R_{2s}[r] = \frac{e^{-\frac{r}{2a_B}}}{2\sqrt{2} a_B^{3/2}} \left(2 - \frac{r}{a_B} \right);$$

it follows, up to order $(R/a_B)^3$,

$$\Delta E_{1s} = \frac{2}{5} \left(\frac{R}{a_B} \right)^2 \frac{e^2}{a_B} \equiv \frac{2}{5} \left(\frac{R}{a_B} \right)^2 \text{ a.u.}; \quad \Delta E_{2s} = \frac{1}{20} \left(\frac{R}{a_B} \right)^2 \frac{e^2}{a_B} \equiv \frac{1}{20} \left(\frac{R}{a_B} \right)^2 \text{ a.u.}$$

Energy shift for states with higher L are depressed, since radial wave functions decrease as r^L . For p states we expect $\Delta E \sim (R/a_B)^4 \text{ a.u.}$, as is easily confirmed for example computing the correction to $2p$ state:

$$R_{2p}[r] = \frac{e^{-\frac{r}{2a_B}} r}{2\sqrt{6} a_B^{5/2}}; \quad \Delta E_{2p} = \frac{e^2 R^4}{1120 a_B^5} + O[R]^5 \approx \frac{1}{1120} \left(\frac{R}{a_B} \right)^4 \text{ a.u.}$$

□ A different approach

Let us call $e\rho$ the charge density of the nucleus, or in general $Z e\rho$ for a nucleus with Z protons. If V is the electrostatic potential we can write the generic energy shift as

$$\Delta E = -e \int d^3 \mathbf{r} |\psi[r]|^2 \left(V - \frac{Ze}{r} \right) \approx -e |\psi[0]|^2 \int d^3 \mathbf{r} \left(V - \frac{Ze}{r} \right). \quad (2.3)$$

Last approximate equality take care of the fact that V differ from Z/r only at very small distances, and clarify that in practice only s -states are affected by the perturbation. Using the identity

$$1 = \frac{1}{6} \Delta r^2,$$

and integrating by parts eq (3) can be rewritten as

$$\Delta E = -e |\psi[0]|^2 \int d^3 \mathbf{r} \frac{1}{6} r^2 \Delta \left(V - \frac{Ze}{r} \right) = -e |\psi[0]|^2 \frac{1}{6} \int d^3 \mathbf{r} r^2 (4\pi e\rho - Ze 4\pi \delta^3[\mathbf{r}]) = \frac{2}{3} \pi Z |e|^2 |\psi[0]|^2 \langle r^2 \rangle.$$

The measure of ΔE would be a direct measure of mean square radius of the (charge of the) nucleus.

Problem 3

Let us suppose that Coulomb potential has a behaviour $1/r^{1+\varepsilon}$, with $\varepsilon \ll 1$. Compute the effect on hydrogen levels and derive a bound on ε comparing the $2p$ - $2s$ induced energy gap with the observed Lamb shift correction. The theory agree with experiment at least up to $\delta E/h = 10^4 \text{ kHz}$.

● Solution

□ Hamiltonian and perturbation

In this problem we will use atomic units $|e| = \hbar = m = 1$. We can consider the difference between the supposed Coulomb law and usual $-1/r$ law as a perturbation

$$H_I = - \left(\frac{1}{r^{1+\varepsilon}} - \frac{1}{r} \right).$$

Energy corrections are given by the mean value of H_I on eigenfunctions of hydrogen atom. Radial wave functions for $1s$, $2s$, $2p$ states are, in atomic units:

$$R_{1s}[r] = 2 e^{-r}; \quad R_{2s}[r] = \frac{e^{-r/2} (2-r)}{2\sqrt{2}}; \quad R_{2p}[r] = \frac{e^{-r/2} r}{2\sqrt{6}}.$$

A simple integration gives (energies in atomic units)

$$\Delta E_{1s} = 2^\varepsilon \Gamma(2-\varepsilon) - 1; \quad \Delta E_{2s} = \frac{1}{8} \left((\varepsilon^2 - \varepsilon + 2) \Gamma(2-\varepsilon) - 2 \right); \quad \Delta E_{2p} = \frac{1}{24} (\Gamma(4-\varepsilon) - 6).$$

Γ is the Euler Gamma function. For small ε a Taylor expansion gives

$$\Delta E_{2s} - \Delta E_{2p} \approx \frac{\varepsilon}{12} \text{ a.u.} = \frac{\varepsilon}{6} \text{ Ry.}$$

The agreement between theory and experiment for the computed Lamb shift between $2s_{1/2}$ and $2p_{1/2}$ levels imply the bound

$$|\varepsilon| < 6 \cdot 10^4 \text{ kHz h} / \text{Ry} \approx 1.8 \cdot 10^{-11}.$$

It can be useful to note the following conversion factors (h is Planck constant, i.e. $2\pi \hbar$)

$$\frac{Ry}{h} = 3\,289\,841.9680 \text{ GHz}; \quad \frac{Ry}{hc} \approx \frac{1.09737 \times 10^7}{\text{Meter}} = \frac{1.09737 \times 10^5}{\text{cm}}. \quad (3.1)$$

Problem 4

Compute the effect of an electric field on the levels of a charged harmonic oscillator. Compute induced electric dipole and verify Feynman-Hellmann theorem.

● Solution

□ Hamiltonian and perturbation

This is the simplest model for studying the effect of an electric field on a quantum system. Let us denote by \mathcal{E} the external electric field and by e the charge of the oscillator. The Hamiltonian is

$$H = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 q^2 - e \mathcal{E} q = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 \left(q - \frac{e \mathcal{E}}{m \omega^2} \right)^2 - \frac{1}{2} \frac{e^2 \mathcal{E}^2}{m \omega^2} \quad (4.1)$$

The change of variable

$$P = p; \quad Q = q - \frac{e \mathcal{E}}{m \omega^2}$$

is a unitary (and classically canonical) transformation, then the physics do not change and we can consider as Hamiltonian

$$H = \frac{P^2}{2m} + \frac{1}{2} m \omega^2 Q^2 - \frac{1}{2} \frac{e^2 \mathcal{E}^2}{m \omega^2}; \quad (4.2)$$

which differ from unperturbed hamiltonian only by an additive constant. All levels are shifted by the same \mathcal{E} dependent constant

$$\Delta E = - \frac{1}{2} \frac{e^2 \mathcal{E}^2}{m \omega^2}. \quad (4.3)$$

The reader can check the result in perturbation theory as an exercise (see also prob.[1]). Let us make some comments on this seemingly trivial exercise.

- The unperturbed system is invariant under parity, $q \rightarrow -q$ and the system, as must be well known by the reader, has no dipole moment in stationary states.
- The perturbed system is *not* parity invariant and the system has a dipole in stationary states (classically an induced dipole). The Hamiltonian (2) is invariant under the transformation $Q \rightarrow -Q$, which is not the parity of the system. By this symmetry the mean value of Q on stationary states of (2) is zero. On exact stationary states, i.e. eigenstates of (2), we have the induced dipole (use the definition of Q):

$$\langle \psi | d | \psi \rangle \equiv e \langle \psi | q | \psi \rangle = e \langle \psi | Q | \psi \rangle + e \left\langle \psi \left| \frac{e \mathcal{E}}{m \omega^2} \right| \psi \right\rangle = \frac{e^2 \mathcal{E}}{m \omega^2}.$$

- The coefficient of proportionality between induced dipole and external field has dimension of a volume and is called *polarizability* of the system. In our case

$$d = \alpha \mathcal{E}; \quad \alpha = \frac{e^2}{m \omega^2}.$$

- Interaction lower energy of the system, see (3), and is written in the same form as classical dipole induced interaction:

$$\Delta E = - \frac{1}{2} \frac{e^2 \mathcal{E}^2}{m \omega^2} = - \frac{1}{2} \alpha \mathcal{E}^2$$

We can verify in this simple system Feynman - Hellmann theorem, which reads in this case

$$\frac{\partial \Delta E}{\partial \mathcal{E}} = \left\langle \psi \left| \frac{\partial H}{\partial \mathcal{E}} \right| \psi \right\rangle. \quad (4.4)$$

The l.h.s. of (4) is $-\alpha \mathcal{E}$. The r.h.s. is:

$$\left\langle \psi \left| \frac{\partial H}{\partial \mathcal{E}} \right| \psi \right\rangle = - e \langle \psi | q | \psi \rangle = - \frac{e^2 \mathcal{E}}{m \omega^2} = - \alpha \mathcal{E},$$

verifying the theorem.

Problem 5

Solve the two level system

$$H = E_0 + \begin{pmatrix} -E_1 & -\delta \\ -\delta^* & E_1 \end{pmatrix} \equiv E_0 - \boldsymbol{\sigma} \cdot \mathbf{B}$$

and compare with perturbation theory results as $\mathbf{B} \rightarrow 0$. Discuss how the phases of eigenstates depend on \mathbf{B} .

Solution

Exact solution

Our problem has only two states, conventionally denoted by $| \uparrow \rangle$ and $| \downarrow \rangle$. The constant E_0 given in the text of the exercise is just an additive constant to the energy and will be disregarded from now on. The Hamiltonian can be considered in a form

$$H = H_0 + V; \quad H_0 = \begin{pmatrix} -E_1 & 0 \\ 0 & E_1 \end{pmatrix}; \quad V = \begin{pmatrix} 0 & -\delta \\ -\delta^* & 0 \end{pmatrix}; \tag{5.1}$$

and studied exactly or with perturbation theory. The eigenvalues are trivially found solving the quadratic equation $\det(\lambda - H) = 0$, but as an exercise we want to follow another more instructive path. System (1) can be considered as the Hamiltonian of a spin 1/2 interacting with a magnetic field. Magnetic interaction for spin 1/2 is described by $-\mu \boldsymbol{\sigma} \cdot \mathbf{B}$ where μ is the magnetic moment, \mathbf{B} the magnetic field and $\boldsymbol{\sigma}$ the Pauli matrices. With the substitution $\mathbf{B} \rightarrow \mu \mathbf{B}$ our system is indeed a magnetic Hamiltonian. If we write

$$\delta = \Delta e^{-i\varphi}; \quad H = -\boldsymbol{\sigma} \cdot \mathbf{B}; \quad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{5.2}$$

we have

$$H = - \begin{pmatrix} E_1 & (\Delta \cos[\varphi] - i \Delta \sin[\varphi]) \\ (\Delta \cos[\varphi] + i \Delta \sin[\varphi]) & -E_1 \end{pmatrix},$$

and we can identify the components of our magnetic field with

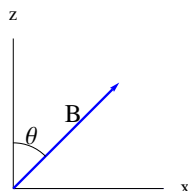
$$B_x = \Delta \cos[\varphi]; \quad B_y = \Delta \sin[\varphi]; \quad B_z = E_1; \quad B = |\mathbf{B}| = \sqrt{\Delta^2 + E_1^2}. \tag{5.3}$$

In our magnetic analogy the perturbation treatment would consist in adding a transverse magnetic field of strength Δ to a magnetic field E_1 along z (the direction of the magnetic field is what identify z direction). In this language it is clear that we can choose the x direction along the transverse field and put $\varphi = 0$, i.e. kill y -component of \mathbf{B} field. From now on we adopt this convention and write $\Delta \in \mathbb{R}$ instead of δ . Let us note that we can also choose $\varphi = \pi$, than have in effect both positive and negatives vaules for Δ . A priori the two choices are distinct and this will have some consequence below.

The reader now has 3 choices, he can forget this discussion and assume from the beginning a real Hamiltonian, or he can read the note at the end of this subsection to understand for a generic system (without a real magnetic field) what it means the choice δ real. The third (better) choice is to try to understand by himself the question.

In the real form H is given by

$$H = - \begin{pmatrix} E_1 & \Delta \\ \Delta & -E_1 \end{pmatrix} = -\sigma_x B_x - \sigma_z B_z = -B \begin{pmatrix} \cos[\theta] & \sin[\theta] \\ \sin[\theta] & -\cos[\theta] \end{pmatrix}.$$



$$B_x = B \sin[\theta]; \quad B_z = B \cos[\theta]; \quad \sin[\theta] = \frac{\Delta}{B}; \quad B = \sqrt{E_1^2 + \Delta^2} \tag{5.4}$$

and it is apparent that we can diagonalize the Hamiltonian by bringing z axis along \mathbf{B} . The rotation of reference frame is an anticlockwise rotation around y axis, i.e.

$$R = \text{Exp}\left[i \frac{\theta}{2} \sigma_y\right] = \cos\left[\frac{\theta}{2}\right] + i \sigma_y \sin\left[\frac{\theta}{2}\right] = \begin{pmatrix} \cos\left[\frac{\theta}{2}\right] & +\sin\left[\frac{\theta}{2}\right] \\ -\sin\left[\frac{\theta}{2}\right] & \cos\left[\frac{\theta}{2}\right] \end{pmatrix} \tag{5.5}$$

In the rotated basis the Hamiltonian will be diagonal, and in effect the reader can check that

$$R H R^\dagger = -B \sigma_z. \tag{5.6}$$

The new basis vectors will be

$$|g\rangle = R^\dagger |+\rangle = \begin{pmatrix} \cos\left[\frac{\theta}{2}\right] & -\sin\left[\frac{\theta}{2}\right] \\ +\sin\left[\frac{\theta}{2}\right] & \cos\left[\frac{\theta}{2}\right] \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} \cos\left[\frac{\theta}{2}\right] \\ \sin\left[\frac{\theta}{2}\right] \end{pmatrix}; \quad |e\rangle = R^\dagger |-\rangle = \begin{pmatrix} -\sin\left[\frac{\theta}{2}\right] \\ \cos\left[\frac{\theta}{2}\right] \end{pmatrix}. \quad (5.7)$$

N.B. We remember that basis vectors transform as the inverse rotation, see notebook [**] for more details.

The reader can verify directly that

$$H |g\rangle = -B |g\rangle; \quad H |e\rangle = B |e\rangle; \quad (5.8)$$

$|g\rangle$ and $|e\rangle$ are respectively the ground state and the excited state of the system with energy eigenvalues $\mp B = \mp \sqrt{E_1^2 + \Delta^2}$

□ The choice of initial phases

The reader can skip this subsection in a first reading.

The thesis is that we can always choose the phases of our states in such a way that δ is real. This is trivially true in the sense that if we choose as basis vectors

$$|a\rangle = e^{-i\varphi/2} |+\rangle; \quad |b\rangle = e^{+i\varphi/2} |-\rangle; \quad (5.9)$$

the Hamiltonian has the same diagonal matrix elements

$$\langle a | H | a \rangle = \langle + | H | + \rangle = -E_1; \quad \langle b | H | b \rangle = \langle - | H | - \rangle = E_1;$$

and real off diagonal elements

$$\langle a | H | b \rangle = e^{i\varphi} \langle + | H | - \rangle = -\Delta; \quad \langle b | H | a \rangle = e^{-i\varphi} \langle - | H | + \rangle = -\Delta.$$

The choice of the phase of basis functions can always be made by a unitary transformation so the physics is not changed. Let us note that $|a\rangle$ and $|b\rangle$ are obtained from $|+\rangle$ and $|-\rangle$ states by the unitary transformation $\text{Exp}[-i\varphi/2 \sigma_z]$:

$$|a\rangle = \text{Exp}[-i\varphi \sigma_z / 2] |+\rangle; \quad |b\rangle = \text{Exp}[-i\varphi \sigma_z / 2] |-\rangle;$$

and this is exactly how a rotation of an angle φ acts on spinors in the magnetic analogy.

From a physical point of view we can state the same conclusions with a different perspective. In two dimensions we have only 4 independent hermitian matrices, the identity and the four Pauli matrices, each matrix can be written as a linear superposition of these matrices. The "maximal abelian set" of observables, neglecting identity, is formed by only one element, one of the Pauli matrices, by convention let us choose σ_z . Our states are labeled by eigenvalues of this observable, nothing else, and in effect the two states $|a\rangle$ and $|b\rangle$ for example belong to the same eigenvalue of σ_z .

To pass from rays to vectors in Hilbert space we have to make a choice for phases, and this means to choose $|a\rangle$ and $|b\rangle$. To avoid misunderstandings this does not mean that we can change the phases in such a way that every linear combination $|\psi\rangle = c_1 |a\rangle + c_2 |b\rangle$ has real coefficients: once we have chosen a phase for basis vectors this choice is valid for every linear combination.

There is one more subtle point. When we write σ matrices in the usual form we have in effect done a choice of phases, for example σ_y has purely imaginary elements, how this combine with the above freedom in phases? In effect when we have stated in the main text that the usual representation of spin 1/2 is The representation of SU(2) of dimension 2 it was understood up to unitary transformations. Which means again that we can always choose the phases in such a way the σ matrices have the usual form. Now if we do a unitary transformation on a basis which satisfy usual convention on the phases we obtain again a representation with the correct phases. In effect the only point is the state $|a\rangle$ which is defined, without additional phases, as $(\sigma_x - i\sigma_y)/2$. If we perform a unitary transformation both matrices and states change. Under the transformation $R = \text{Exp}[-i\varphi \sigma_z / 2]$ for example:

$$\sigma_i \rightarrow \Sigma_i = R \sigma_i R^\dagger$$

and under a unitary transformation all linear relation, and commutation relations, remain invariant, in particular the new $|a\rangle$ state, which is $|b\rangle$ obtained by applying the new sigma matrices, Σ , to $|a\rangle$ and everything works in exactly the same way.

In effect after the transformation we had to write Σ instead of σ for matrices and spin operators, but as these operators on the new basis have the same matrix elements as old operators in the old basis we use the same symbols, as is always more or less implicitly done.

■ Non degenerate perturbation theory

Simple perturbation theory on non degenerate levels can be applied for $\Delta \ll E_1$. In absence of perturbation $-B \sin[\theta]$ ground and excited state are $|+\rangle$ and $|-\rangle$. As $\langle + | \sigma_x | + \rangle = 0 = \langle - | \sigma_x | - \rangle$ corrections to eigenvalues start from second order and we have

$$\Delta E_g = -E_1 + \Delta^2 \langle + | \sigma_x | - \rangle \frac{1}{-2E_1} \langle - | \sigma_x | + \rangle = -E_1 \left(1 + \frac{1}{2} \frac{\Delta^2}{E_1^2} \right);$$

$$\Delta E_e = E_1 + \Delta^2 \langle + | \sigma_x | - \rangle \frac{1}{2E_1} \langle - | \sigma_x | + \rangle = E_1 \left(1 + \frac{1}{2} \frac{\Delta^2}{E_1^2} \right).$$

These results are in agreement with Taylor expansion of exact results (8), as for small Δ

$$B = \sqrt{E_1^2 + \Delta^2} \approx E_1 \left(1 + \frac{1}{2} \frac{\Delta^2}{E_1^2} \right).$$

The eigenstates have a first order correction. Using the general formula

$$\delta |n\rangle = \sum_{s \neq n} \frac{1}{E_n - E_s} |s\rangle \langle s | V | n \rangle,$$

we have for first order eigenstates with $V = -\Delta \sigma_x$:

$$|g\rangle \approx |+\rangle + \frac{\Delta}{2 E_1} |-\rangle \approx |+\rangle + \frac{\theta}{2} |-\rangle; \quad |e\rangle \approx |-\rangle - \frac{\Delta}{2 E_1} |+\rangle \approx |-\rangle - \frac{\theta}{2} |+\rangle;$$

which are first order expansion of (7).

■ **Degenerate perturbation theory**

As $E_1 \rightarrow 0$, and in general for $|E_1| \ll \Delta$ previous formulae do not apply and in this regime we have to switch to degenerate perturbation theory. To see exactly why perturbation theory on degenerate levels is different let us consider the exact solution (7). As $\tan[\theta] = \Delta / E_1$ we see that the value of θ in the degeneration limit $E_1 \rightarrow 0$ depends on the sign of Δ

$$\lim_{E_1 \rightarrow 0} \theta = \begin{cases} \pi / 2; & \text{if } \Delta / E_1 > 0 \\ -\pi / 2; & \text{if } \Delta / E_1 < 0 \end{cases}$$

Accordingly for ground state, as an example

$$\lim_{E_1 \rightarrow 0^+} |g\rangle = \begin{cases} (|+\rangle + |-\rangle) / \sqrt{2} \equiv |S\rangle; & \text{if } \Delta > 0 \\ (|+\rangle - |-\rangle) / \sqrt{2} \equiv |A\rangle; & \text{if } \Delta < 0 \end{cases}$$

i.e. when we switch off the perturbation Δ we do not know in advance which state of the two dimensional space spanned by $|+\rangle$ and $|-\rangle$ correspond to ground and excited state.

States $|S\rangle$ and $|A\rangle$ diagonalize the degenerate hamiltonian but we see that $|g\rangle$ is not analytic in Δ , precisely is discontinuous for $\Delta = 0$. A similar thing happens for eigenvalues. In the degenerate limit eigenvalue are $\pm |\Delta|$ which are continuous but not derivable in $\Delta = 0$.

This picture has some relevant consequences. If we imagine to vary smoothly the external field, the eigenvectors follow the variation except if we pass through the singular point $E_1 = 0, \Delta = 0$, where there is an abrupt change. This is why adiabatic theorem does not work if in the evolution the system goes through a degeneracy point.

This breaking of adiabatic theorem is even more clear if we switch on the y component of the magnetic field. In the general case

$$B_x = B \sin[\theta] \cos[\varphi]; \quad B_y = B \sin[\theta] \sin[\varphi]; \quad B_z = B \cos[\theta]; \quad B = \sqrt{E_1^2 + \Delta^2};$$

As already noted the y component can be reabsorbed by an anticlockwise rotation of φ around z axis of the reference frame. After rotation the new unperturbed eigenstates will be

$$|+\rangle' = R_z^\dagger[\varphi] |+\rangle = \text{Exp}\left[-i \frac{\varphi}{2} \sigma_z\right] |+\rangle = \text{Exp}\left[-i \frac{\varphi}{2}\right] |+\rangle; \quad |-\rangle' = \text{Exp}\left[+i \frac{\varphi}{2}\right] |-\rangle. \tag{5.10}$$

For these states everything works as before the only difference being that now Δ , the modulus of transverse field, is necessarily positive. In the degenerate limit

$$|g\rangle = \frac{1}{\sqrt{2}} (|+\rangle' + |-\rangle') = \frac{1}{\sqrt{2}} \begin{pmatrix} \text{Exp}\left[-i \frac{\varphi}{2}\right] \\ \text{Exp}\left[+i \frac{\varphi}{2}\right] \end{pmatrix}.$$

The ground state has now a continuous range of variation, not only a double determination as before. Which of the infinite set correspond to the true ground state depends on the actual value of φ .

The general solution, see (7), is

$$|g\rangle = \cos\left[\frac{\theta}{2}\right] |+\rangle' + \sin\left[\frac{\theta}{2}\right] |-\rangle' = \begin{pmatrix} \cos\left[\frac{\theta}{2}\right] \text{Exp}\left[-i \frac{\varphi}{2}\right] \\ \sin\left[\frac{\theta}{2}\right] \text{Exp}\left[+i \frac{\varphi}{2}\right] \end{pmatrix}. \tag{5.11}$$

We note that $|g\rangle$ change its sign as φ varies from 0 to 2π , like spinor (we remember that in principle our system has nothing to do with a real spinor). This effect is a particularly simple form of Berry phase.

Consider a system in which we vary adiabatically the transverse field around a circle, i.e. φ varies from 0 to 2π . In principle we can locally adjust the phase of our eigenstates in such a way that the ground state follows the variation of the field, why we obtain an additive minus sign after a circle? Let us consider the infinitesimal variation of the state under a change of a set of parameters λ_i

$$\langle g | \frac{\partial}{\partial \lambda_i} | g \rangle \quad (5.12)$$

if we can reset to zero expression (12) with a change of phase, then we can choose our phases in such a way that they follow variations of external field. In the present case our parameters are θ and φ and we have from (11)

$$\langle g | \frac{\partial}{\partial \theta} | g \rangle = 0; \quad \langle g | \frac{\partial}{\partial \varphi} | g \rangle = -\frac{i}{2} \cos[\theta].$$

Consider now a totation of the transverse field at fixed θ . To reabsorb the phase variation we would need a change of phase

$$| g \rangle \rightarrow \text{Exp}[i \alpha] | g \rangle; \quad \alpha[\varphi] = \frac{1}{2} \cos[\theta] \varphi,$$

but the function α is not monodrome in φ , i.e. is not a function, so it is not allowed, and we cannot reabsorb the phase variation in a closed loop by a global defined α . The amount of phase change under a cyclic variation of external condition is substantially the Berry phase of the system.

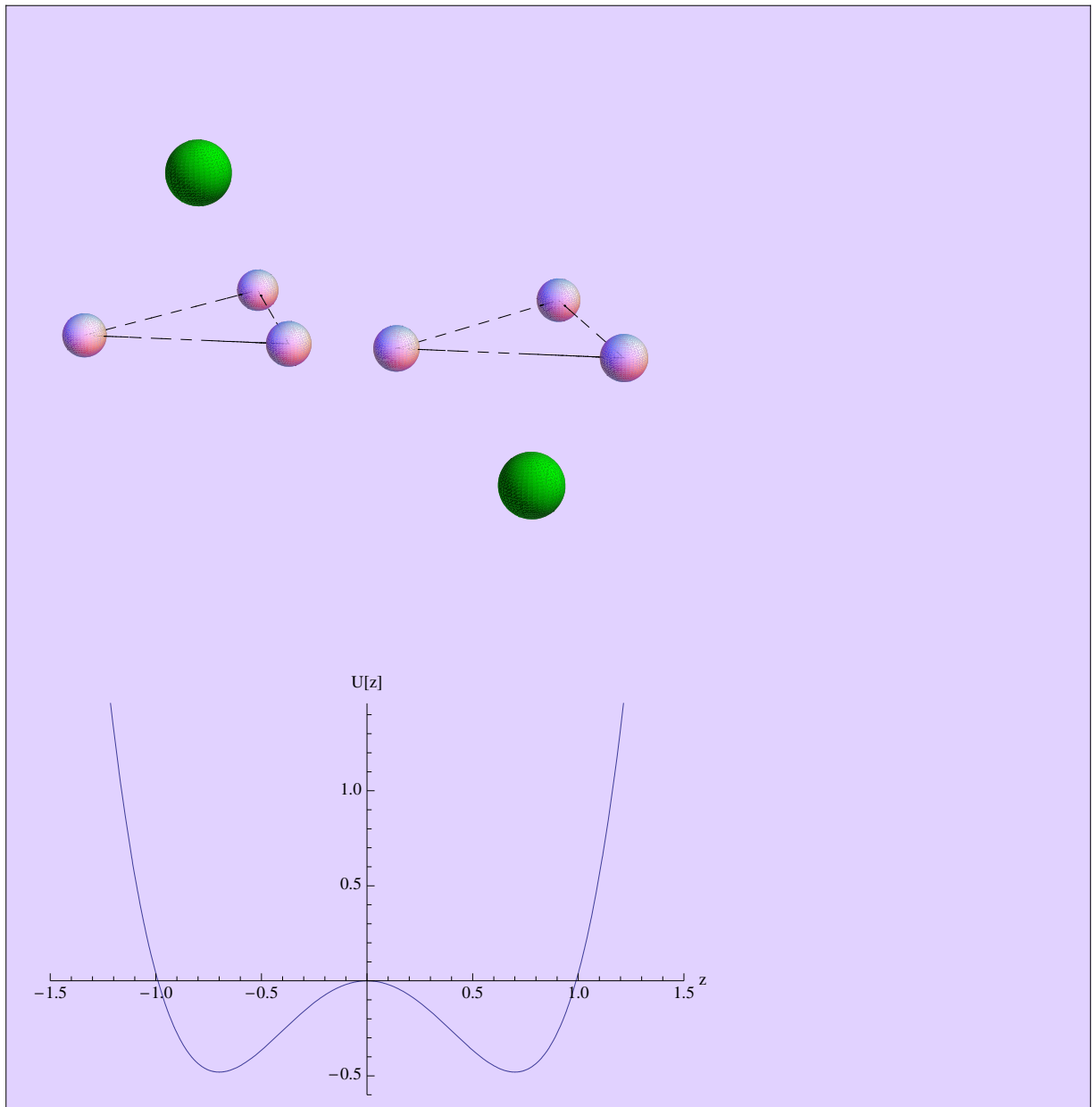
Problem 6

A two level system as that of problem [5] can be considere as a simplified model of an ammonia molecule, NH_3 . Nitrogen's position with respect to the plane of 3 hydrogen atoms select, classically, two equivalent configuration. Define a parity operator for this model and discuss its property. Study the effect of an electric field on the system.

● Solution

■ Description of the model

An ammonia molecule can be described by three coplanar hydrogen atoms, (x,y) plane, and a nitrogen outside the plane. The system admits a specular configuration obtained by a reflection across (x,y) plane, i.e. $z \rightarrow -z$, then a second position for nitrogen atom, classically equivalent to the first one, exists. Classically the two position are separated by a potential barrier, and are local minima of the potential energy. Tunnel effect allow a mixing between these two configurations. The situation is described pictorially inthe folowing figure:



Neglecting tunnel effects an effective Hamiltonian for the system can be taken as

$$H_0 = \begin{pmatrix} E_0 & 0 \\ 0 & E_0 \end{pmatrix}; \quad P = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \quad (6.1)$$

The basis states correspond to classically localized states, $|+\rangle$ and $|-\rangle$ and P is the operator which exchange these states, i.e. parity. Tunnel effect produce an amplitude different from zero for the transition between the two states and can be added to H_0 in the form of off diagonal terms

$$H = \begin{pmatrix} E_0 & -\Delta \\ -\Delta & E_0 \end{pmatrix}. \quad (6.2)$$

This is exactly the Hamiltonian considered in previous exercise, with $E_1 = 0$, and the two eigenstates are

$$|g\rangle = \frac{1}{\sqrt{2}} (|+\rangle + |-\rangle) \equiv |S\rangle; \quad |e\rangle = \frac{1}{\sqrt{2}} (|+\rangle - |-\rangle) \equiv |A\rangle; \quad (6.3)$$

Let us notice that for a one dimensional problem we now that ground state is symmetric, then in effect $|g\rangle$ is the ground state. This state is even under parity, $P|g\rangle = |g\rangle$ while excited state is odd.

- A question for the reader: the sign of Δ depends on the choice of the relative phase between $|+\rangle$ and $|-\rangle$ states. How this is consistent with the assertion that ground state for a one dimensional potential must be symmetric?

■ Electric field

The charge distribution in configurations $|+\rangle$ and $|-\rangle$ is asymmetric, due to greater electronegativity of Nitrogen. Classically this means that these states possess an electric dipole. We can describe this effect with

$$\mathbf{d} = \langle + | \mathbf{e}_z | + \rangle; \quad -\mathbf{d} = \langle - | \mathbf{e}_z | - \rangle; \quad \langle - | \mathbf{e}_z | + \rangle = 0; \quad (6.4)$$

We note that the first equality is a definition, while the other two equalities are a consequence of our model.

Let us assume that our states are (relatively) real, e.g. are approximate real solution of one dimensional Schrödinger equation. The parity operator P must act on z as $P z P^{-1} \equiv P z P = -z$ (we used $P^2 = 1$), then

$$\langle - | z | - \rangle = \langle + | P z P | + \rangle = -\langle + | z | + \rangle = -\mathbf{d}.$$

For the third equality, using reality of matrix elements:

$$\langle - | z | + \rangle = \langle + | P z P | - \rangle = -\langle + | z | - \rangle = -(\langle - | z | + \rangle)^* = -\langle - | z | + \rangle \Rightarrow \langle - | z | + \rangle = 0.$$

Let us note that states $|+\rangle$ and $|-\rangle$ are not eigenstates of Hamiltonian (2) so the general theorem about absence of electric dipole moment on stationary states do not apply. If we neglect tunneling the states are eigenstates of (1) but the system is degenerate and again the theorem does not apply.

If we switch on an electric field \mathcal{E} , this field will couple with dipole moment and the Hamiltonian becomes

$$H = E_0 + \begin{pmatrix} -d\mathcal{E} & -\Delta \\ -\Delta & d\mathcal{E} \end{pmatrix}. \quad (6.5)$$

The Hamiltonian (5) is identical to that of problem [5] and we can write at once energy levels and eigenstates:

$$E = E_0 \mp \sqrt{\Delta^2 + d^2 \mathcal{E}^2}; \quad |g_{\mathcal{E}}\rangle = \begin{pmatrix} \cos\left[\frac{\theta}{2}\right] \\ \sin\left[\frac{\theta}{2}\right] \end{pmatrix}; \quad |e_{\mathcal{E}}\rangle = \begin{pmatrix} -\sin\left[\frac{\theta}{2}\right] \\ \cos\left[\frac{\theta}{2}\right] \end{pmatrix}; \quad \tan[\theta] = \frac{\Delta}{d\mathcal{E}}. \quad (6.6)$$

Equation (6) explain in a simple way how in quantum mechanics we can have approximately a linear Stark effect, which mimics the classical interaction $-d\mathcal{E}$. In the limit of large fields with respect the transition matrix element, or energy splitting, $d\mathcal{E} \gg \Delta$, we have $\theta \rightarrow 0$ and

$$E = E_0 \mp d\mathcal{E}; \quad |g\rangle_{\mathcal{E}} \approx \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \quad |e\rangle_{\mathcal{E}} \approx \begin{pmatrix} 0 \\ 1 \end{pmatrix};$$

We have classical linear dependency on electric field which mimics a permanent dipole of the system. Eigenstates are "frozen" toward classical localized states. In these states, see eq.(4)

$$\langle g_{\mathcal{E}} | \mathbf{e}_z | g_{\mathcal{E}} \rangle \approx \mathbf{d}; \quad \langle e_{\mathcal{E}} | \mathbf{e}_z | e_{\mathcal{E}} \rangle \approx -\mathbf{d}.$$

In effect permanent static dipole, polarizability etc, are defined in the limit of vanishing external field. Let us assume $d\mathcal{E} \rightarrow 0^+$, then $\theta \rightarrow \pi/2$ and we have

$$E = E_0 \mp \left(\Delta + \frac{1}{2} \frac{d^2 \mathcal{E}^2}{\Delta} \right); \quad (6.7)$$

$$|g_{\mathcal{E}}\rangle = \frac{1}{\sqrt{2}} \left(\left(1 + \frac{d\mathcal{E}}{2\Delta} \right) |+\rangle + \left(1 - \frac{d\mathcal{E}}{2\Delta} \right) |-\rangle \right);$$

$$|e_{\mathcal{E}}\rangle = \frac{1}{\sqrt{2}} \left(\left(1 - \frac{d\mathcal{E}}{2\Delta} \right) |-\rangle - \left(1 + \frac{d\mathcal{E}}{2\Delta} \right) |+\rangle \right);$$

From eq.(7) we see that Stark effect is indeed quadratic with polarizations

$$E - E_0 = -\frac{1}{2} \alpha \mathcal{E}^2; \quad \alpha_g = \frac{d^2}{\Delta}; \quad \alpha_e = -\frac{d^2}{\Delta}.$$

We note that for excited states polarizability has a negative sign, so the atoms behave at the opposite of usual dielectrics (they are repelled in an external gradient field).

These results are confirmed by taking the mean value of the dipole operator on exact eigenstates in the limit of small field:

$$\langle g_{\mathcal{E}} | \mathbf{e}_z | g_{\mathcal{E}} \rangle \approx \frac{d^2}{\Delta} \mathcal{E}; \quad \langle e_{\mathcal{E}} | \mathbf{e}_z | e_{\mathcal{E}} \rangle \approx -\frac{d^2}{\Delta} \mathcal{E}.$$

Problem 7

Study the effect of an electric field (Lo Surdo-Stark effect) on the $n=2$ states of the hydrogen atom, neglecting the effects of spin.

Solution

General properties

In the non relativistic approximation the $n=2$ level of hydrogen atom has degeneration 4, (we neglect spin degrees of freedom): there is one 2s state and three 2p states. Let us choose as quantization axis (z axis) the direction of the electric field \mathcal{E} . The Hamiltonian is

$$H = \frac{p^2}{2m} - \frac{e^2}{r} - e z \mathcal{E} \quad (7.1)$$

e is the electron charge. H is invariant for rotations around z axis, then L_z can be diagonalized simultaneously with H . In perturbation theory this is reflected by the fact that the term $e z \mathcal{E}$ has no matrix elements between states with different eigenvalues of L_z .

The Hamiltonian is also invariant under reflection \mathcal{R} across a plane containing z axis, ex. $y \rightarrow -y$. Classically the projections of angular momentum along z change sign under this operation, the same is true in quantum theory. In angular coordinates this symmetry is equivalent to $\varphi \rightarrow -\varphi$ and with our choice of phase for spherical harmonics

$$Y_L^m(\vartheta, -\varphi) = (-1)^m Y_L^{-m}(\vartheta, \varphi); \Rightarrow \mathcal{R} |n, L, m\rangle = (-1)^m |n, L, -m\rangle. \quad (7.2)$$

As H commutes with \mathcal{R} the states with opposite m (eigenvalue of L_z) will remain degenerate even in presence of the perturbation. The same conclusion can be drawn using time reversal symmetry and the relation

$$Y_L^{-m}(\vartheta, \varphi) = (-1)^m Y_L^m(\vartheta, \varphi)^*$$

Perturbation theory

Perturbation theory on $n = 2$ level is a typical example of degenerate perturbation theory and we have to diagonalize matrix elements of the perturbation on the subspace spanned by states 2s, 2p. We have seen some selection rules in previous section, to this we add that z is *odd* with respect parity, so only matrix elements between *different* parity can be different from zero.

Denoting the states with $|2s\rangle, |2p, m\rangle$, where m is the eigenvalue of L_z , at first order the selection rule on L_z imply the following form block diagonal form for perturbation:

$$-e \mathcal{E} \begin{pmatrix} 0 & \langle 2s | z | 2p, 0 \rangle & 0 & 0 \\ \langle 2p, 0 | z | 2s \rangle & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} = -e \mathcal{E} \begin{pmatrix} 0 & a & 0 & 0 \\ a & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}.$$

We see that energy of states $|2p, 1\rangle$ are left unchanged by the perturbation, its only effect is a mixing between $|2s\rangle$ and $|2p, 0\rangle$ states. Wave functions for these states are

$$\psi_{2s} = R_{20} Y_{00} = \frac{1}{a^{3/2} \sqrt{8\pi}} \text{Exp}\left[-\frac{r}{2a}\right] \left(1 - \frac{r}{2a}\right);$$

$$\psi_{2p,0} = R_{21} Y_{20} = \frac{1}{a^{3/2}} \frac{1}{2\sqrt{6}} \frac{r}{a} \text{Exp}\left[-\frac{r}{2a}\right] \sqrt{\frac{3}{4\pi}} \text{Cos}[\theta];$$

a is the Bohr radius. An easy integral gives

$$\langle 2s | -e \mathcal{E} z | 2p, 0 \rangle = 3 e \mathcal{E} a.$$

The relevant part of the perturbation to be diagonalized is just the 2x2 matrix

$$3 e \mathcal{E} a \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

Eigenvalues and eigenvectors are

$$E_A = -3 e \mathcal{E} a; \quad \psi_A = \frac{1}{\sqrt{2}} (\psi_{2s} - \psi_{2p,0}); \quad E_B = +3 e \mathcal{E} a; \quad \psi_B = \frac{1}{\sqrt{2}} (\psi_{2s} + \psi_{2p,0}).$$

We have a linear Stark effect due the degeneracy of the $n = 2$ level. States ψ_A and ψ_B are *not* parity eigenstates and admit a dipole moment. From previous matrix elements it follow

$$\langle \psi_A | z | \psi_A \rangle = +3 a; \quad \langle \psi_B | z | \psi_B \rangle = +3 a.$$

Problem 8

A particle moves in a potential U . Let us suppose that we know all the eigenfunctions for this system and that a perturbation $V[x]$ acts on the system. The computation of first order correction to eigenvalues is, in usual cases, reduced to an integral. The computation of first order correction $\psi^{(1)}$ to wave functions involve generically a sum on infinite terms. Show that the problem of finding $\psi^{(1)}$ can be recasted in the form of solving an inhomogenous partial differential equation. Set $\psi^{(1)} = f[x] \psi^{(0)}[x]$ for the first order eigenfunctions and write an equation for f . In particular consider the case of a central potential and a perturbation in the form of a constant electric field. This method of solution is known as Dalgarno-Lewis' method.

● Solution

■ The method

The complete stationary Schrödinger equation for this problem has the form:

$$-\frac{\hbar^2}{2m} \Delta \psi + U \psi + V \psi = E \psi.$$

Let ψ_0 a given eigenstate solution of the unperturbed equation, with eigenvalues E_0 . Let us suppose that the level is non degenerate or that V is diagonal with respect quantum numbers used to classify the eigenstates of the degenerate subspace belonging to eigenvalue E_0 . In these cases the first order correction to energy and eigenstate are given by

$$\epsilon_1 = \int |\psi_0|^2 V d\mathbf{x}; \quad \psi_1 = \sum_{s \neq 0} f_s[x] \frac{1}{E_0 - E_s} \langle s | V | 0 \rangle; \quad (8.1)$$

f_s is the generic name for eigenfunctions. In general is very difficult to compute exactly the infinite sum in (1), in this problem we study a method which reduce this problem to a solution of a differential equation, usually easier to manage. Having computed ψ_1 perturbation theory allows an easy computation of second and third order corrections to energy levels.

let us write $\psi = \psi_0 + \psi_1$ and $E = E_0 + \epsilon_1$ with ψ_1 and ϵ_1 of first order in the perturbation. Neglecting second order quantities in V and using the fact that ψ_0 satisfies unperturbed equation, Schrödinger equation for ψ can be written as

$$-\frac{\hbar^2}{2m} \Delta \psi_1 + U \psi_1 + V \psi_0 = \epsilon_1 \psi_0 + E_0 \psi_1; \quad \text{or} \quad (H_0 - E_0) \psi_1 = (\epsilon_1 - V) \psi_0 \quad (8.2)$$

This is an inhomogenous equation for ψ_1 . Let ϕ one particular solution of this equation, as the operator $H_0 - E_0$ has a nontrivial kernel of dimension 1 (we assume non degeneracy) then the general solution is of the form

$$\psi_1 = \phi + c \psi_0.$$

In perturbation theory the correction to a state is fixed by requiring $\langle \psi_1 | \psi_0 \rangle = 0$, this fixes the constant and the solution is

$$\psi_1 = \phi - \langle \psi_0 | \phi \rangle \psi_0. \quad (8.3)$$

The equation (2) can be simplified with the position $\psi_1 = f \psi_0$. Expanding the derivatives and using equation for ψ_0 we have:

$$-\frac{\hbar^2}{2m} \psi_0 \Delta f - \frac{\hbar^2}{m} \nabla f \cdot \nabla \psi_0 + (V - \epsilon_1) \psi_0 = 0. \quad (8.4)$$

This equation does not contain explicitly the unperturbed potential U .

■ Electric field and central potential

Consider now the particularly important case of a central potential $U[r]$ and a perturbation due to an electric field $V = -e \mathcal{E} z$. We want to compute corrections to the wave function of fundamental state. ψ_0 is spherically symmetric and the perturbation can mix only to states with $L = 1$, $L_z = 1$, odd states, i.e. functions of the form $z \Phi[r]$. The first order correction ϵ_1 is zero for parity. We then put in the general equation (4)

$$f = z F[r].$$

Using (the prime denote a derivative with respect to r)

$$\partial_i \psi_0 = \frac{x_i}{r} \psi_0'; \quad \partial_i (z F) = \delta_{i3} F + z \frac{x_i}{r} F'; \quad \Rightarrow \quad \partial_i \psi_0 \partial_i (z F) = \psi_0' \left(\frac{z}{r} F + z F' \right); \quad \Delta (z F) = 4 \frac{z}{r} F' + z F'';$$

the equation for F becomes

$$-\frac{\hbar^2}{2m} \left(4 \frac{z}{r} F' + z F'' \right) - \frac{\hbar^2}{m} \frac{\psi_0'}{\psi_0} \left(\frac{z}{r} F + z F' \right) - e \mathcal{E} z = 0;$$

i.e.

$$\left(\frac{1}{2} F'' + \frac{2}{r} F' \right) + \frac{\psi_0'}{\psi_0} \left(\frac{F}{r} + F' \right) + e \mathcal{E} \frac{m}{\hbar^2} = 0. \quad (8.5)$$

This equation is valid for *any* central potential, but clearly ψ_0 depends on the problem at hand.

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$$f = \text{Cos}[\theta] F[r]; \quad \psi_1 = \text{Cos}[\theta] F[r] \psi_0[r]. \quad (8.6)$$

In polar coordinates the Laplace operator is (\mathcal{L} is the angular momentum operator)

$$\Delta = \frac{2}{r} \partial_r + \partial_r^2 - \frac{\mathcal{L}^2}{r^2}; \quad \text{and} \quad \mathcal{L} \text{Cos}[\theta] = 2 \text{Cos}[\theta]$$

$\text{Cos}[\theta]$ is proportional to Y_{10} then $\mathcal{L}^2 \text{Cos}[\theta] = 2 \text{Cos}[\theta]$ and equation (2) takes the form (with $\epsilon_1 = 0$)

$$\text{Cos}[\theta] F \left(\frac{\hbar^2}{2m} \Delta \psi_0 + (E_0 - U) \psi_0 \right) + \frac{\hbar^2}{2m} \text{Cos}[\theta] \left(\frac{2}{r} F' \psi_0 + 2 F' \psi_0' + \psi_0 F'' - \frac{2}{r^2} F \psi_0 \right) + e \mathcal{E} r \text{Cos}[\theta] \psi_0 = 0$$

Using Schrödinger equation for ψ_0

$$\left(\frac{1}{2} F'' + \frac{F'}{r} - \frac{F}{r^2} \right) + \frac{\psi_0'}{\psi_0} F' + \frac{e \mathcal{E} m}{\hbar^2} r = 0. \quad (8.7)$$

This equation is valid for *any* central potential, but clearly ψ_0 depends on the problem at hand. Solving this equation we can compute ψ_1 and second order correction to energy is simply an integral

$$\epsilon_2 = \langle \psi_0 | V | \psi_1 \rangle = -e \mathcal{E} \langle \psi_0 | r \text{Cos}[\theta] | \psi_1 \rangle = -\frac{e \mathcal{E}}{3} \int d\mathbf{r} r^2 \psi_0^2 F[r] r.$$

In the last formula we have used the equality $\langle \text{Cos}[\theta]^2 \rangle = 1/3$.

■ Higher orders

Stark effect contain only even powers of angular momentum, and even power of electric field in energy shift, for parity reasons. Equation (6) then generalizes as

$$\psi = \psi_0 + \text{Cos}[\theta] F_1[r] \psi_0[r] + (P_2[\text{Cos}[\theta]] F_{22}[r] + F_{20}[r]) \psi_0 + \dots \quad (8.8)$$

P_L is Legendre polynomial, $\mathcal{L}^2 P_L = -L(L+1) P_L$. By substitution in (2) and using Schrödinger equation for ψ_0 we have now, up to second order and remembering that $\epsilon_1 = 0$:

$$\begin{aligned} & \frac{\hbar^2}{2m} \text{Cos}[\theta] \left(\frac{2}{r} F_1' \psi_0 + 2 F_1' \psi_0' + \psi_0 F_1'' - \frac{2}{r^2} F_1 \psi_0 \right) + \frac{\hbar^2}{2m} P_2 \left(\frac{2}{r} F_{22}' \psi_0 + 2 F_{22}' \psi_0' + \psi_0 F_{22}'' - \frac{6}{r^2} F_{22} \psi_0 \right) \\ & + \frac{\hbar^2}{2m} \left(\frac{2}{r} F_{20}' \psi_0 + 2 F_{20}' \psi_0' + \psi_0 F_{20}'' \right) + e \mathcal{E} r \text{Cos}[\theta] \psi_0 + e \mathcal{E} r \text{Cos}[\theta] (\text{Cos}[\theta] F_1[r] \psi_0) + \epsilon_2 \psi_0 = 0 \end{aligned}$$

We can use

$$\text{Cos}[\theta]^2 = \frac{2 P_2[\text{Cos}[\theta]] + 1}{3}$$

to separate different angular momenta, obtaining, equating similar orders in \mathcal{E} :

$$\begin{aligned} & \left(\frac{1}{2} F_1'' + \frac{1}{r} F_1' - \frac{1}{r^2} F_1 + \frac{\psi_0'}{\psi_0} F_1' \right) + \frac{e \varepsilon m}{\hbar^2} r = 0; \\ & \left(\frac{1}{2} F_{22}'' + \frac{1}{r} F_{22}' - \frac{3}{r^2} F_{22} + \frac{\psi_0'}{\psi_0} F_{22}' \right) + \frac{2}{3} \frac{e \varepsilon m}{\hbar^2} r F_1 = 0; \\ & \left(\frac{1}{2} F_{20}'' + \frac{1}{r} F_{20}' + \frac{\psi_0'}{\psi_0} F_{20}' \right) + \frac{1}{3} \frac{e \varepsilon m}{\hbar^2} r F_1 + \varepsilon_2 \frac{m}{\hbar^2} = 0 \end{aligned} \tag{8.9}$$

Problem 9

Use results of problem [8] to derive the approximate polarizability for a particle moving in a one dimensional potential well of width a and in a radial potential well of radius a with the condition $a\chi \ll 1$, where $\chi = \sqrt{2m|E|/\hbar^2}$, $|E|$ is the binding energy.

● **Solution**

■ **Unidimensional case**

Outside the potential well the unperturbed wave function behaves as

$$\psi_0 = A \text{Exp}[-\chi |x|] \tag{9.1}$$

The condition $a\chi \ll 1$ imply a slow variation inside the well and $\psi_0 \sim A$ for $|x| < a$. In this conditions the contribution to electrostatic energy inside the well can be neglected and the wave function can be taken everywhere in the form (1). In this approximation $A = \sqrt{\chi}$.

We look at first order corrections to ψ_0 due to a perturbation $-e\varepsilon x$, ε is an external electric field. If we write $\psi_1 = f \psi_0$ it has been shown in problem [8] that $f[x]$ satisfy the differential equation

$$\frac{1}{2} f'' + \frac{\psi_0'}{\psi_0} f' + \frac{m e \varepsilon}{\hbar^2} x = 0 \Rightarrow \frac{1}{2} f'' - \chi \varepsilon [x] f' + \frac{m e \varepsilon}{\hbar^2} x = 0. \tag{9.2}$$

With $\varepsilon[x] = \text{Sign}[x]$. A particular solution of this equation is the odd function:

$$f[x] = \frac{1}{2} \frac{m e \varepsilon}{\hbar^2} \left(\frac{x}{\chi^2} + \frac{x^2 \varepsilon[x]}{\chi} \right)$$

The odd function $f \psi_0$ is automatically orthogonal to the even function ψ_0 , then the first order correction to ground state is

$$\psi_1[x] = \frac{1}{2} \frac{m e \varepsilon}{\hbar^2} \left(\frac{x}{\chi^2} + \frac{x^2 \varepsilon[x]}{\chi} \right) \sqrt{\chi} \text{Exp}[-\chi |x|].$$

We can compute second order Stark effect with

$$\Delta E = \langle \psi_0 | V | \psi_1 \rangle = -e \varepsilon \langle \psi_0 | x | \psi_1 \rangle.$$

Performing the integral we have for energy shift and polarizability:

$$\Delta E = -\frac{1}{2} \frac{5}{4} \frac{m e^2 \varepsilon^2}{\hbar^2} \frac{1}{\chi^4}; \quad \Delta E = -\frac{1}{2} \alpha \varepsilon^2 \Rightarrow \alpha = \frac{5}{4} \frac{m e^2}{\hbar^2} \frac{1}{\chi^4}.$$

■ **Three dimensional well**

In the same approximation the wave function of the ground state can be taken as

$$\psi_0 = \sqrt{2\chi} \frac{1}{r} \text{Exp}[-\chi r] \frac{1}{\sqrt{4\pi}} \tag{9.3}$$

We put $\psi_1 = \text{Cos}[\theta] F \psi_0$, see problem [8], and F must satisfy

$$\left(\frac{1}{2} F'' + \frac{F'}{r} - \frac{F}{r^2} \right) + \frac{\psi_0'}{\psi_0} F' + \frac{e \varepsilon m}{\hbar^2} r = 0 \Rightarrow \frac{m \varepsilon e}{\hbar^2} r - \frac{F[r]}{r^2} - \chi F'[r] + \frac{F''[r]}{2} = 0. \tag{9.4}$$

If we look for a polynomial solution we find

$$F[r] = \frac{m \varepsilon e}{\chi \hbar^2} \frac{r^2}{2}$$

and

$$\psi_1 = \cos[\theta] \frac{m \varepsilon e}{\hbar^2} \frac{r^2}{2 \chi} \psi_0.$$

The second order energy shift is

$$\Delta E = - \frac{m \varepsilon^2 e^2}{\hbar^2} \frac{1}{2 \chi} \langle \psi_0 | (r \cos[\theta]) r^2 \cos[\theta] | \psi_0 \rangle = - \frac{1}{2} \frac{m \varepsilon^2 e^2}{\hbar^2} \frac{1}{4 \chi^4}; \quad \alpha = \frac{m \varepsilon^2 e^2}{4 \hbar^2 \chi^4}.$$

Problem 10

Use results of problem [8] to compute the polarizability for an hydrogen atom in the ground state. Give an estimate of the contribution of continuum states.

● Solution

▣ Polarizability

The polarizability α is defined through the expression for energy shift in a constant electric field \mathcal{E} :

$$\Delta E = -\frac{1}{2} \alpha \mathcal{E}^2. \quad (10.1)$$

For parity conservation in unperturbed Hamiltonian, the first order correction to energy level is zero. The second order correction is computed by the general formula

$$\Delta E = \langle \psi_0 | -e \mathcal{E} z | \psi_1 \rangle; \quad (10.2)$$

where ψ_0 and ψ_1 are respectively the unperturbed wave function and its first order correction.

In the following we use atomic units, with $e = \hbar = m = 1$. To come back to usual unities it is sufficient to note that the adimensional expansion parameter is (a is the Bohr radius).

$$\mathcal{F} = e \mathcal{E} a / (e^2 / a).$$

The wave function of ground state hydrogen atom is

$$\psi_0 = \frac{2}{\sqrt{4\pi}} \text{Exp}[-r]. \quad (10.3)$$

To compute ψ_1 we use the results of problem [8]. With

$$\psi_1 = \cos[\theta] F[r] \psi_0 \quad (10.4)$$

F must satisfy, in atomic units,

$$0 = \left(\frac{1}{2} F'' + \frac{F'}{r} - \frac{F}{r^2} \right) + \frac{\psi_0'}{\psi_0} F' + \mathcal{E} r = \left(\frac{1}{2} F'' + \frac{F'}{r} - \frac{F}{r^2} \right) - F' + \mathcal{E} r \quad (10.5)$$

A particular regular solution of this equation is

$$F[r] = \mathcal{E} \left(r + \frac{1}{2} r^2 \right).$$

Inserting this solution in (4) we have ψ_1 . This function is orthogonal to ψ_0 behaving as a angular momentum 1, then no more computations are necessary.

$$\psi_1 = \cos[\theta] \mathcal{E} \left(r + \frac{1}{2} r^2 \right) \psi_0. \quad (10.6)$$

Inserting in (2) we obtain easily

$$\Delta E = -\frac{9}{4} \mathcal{E}^2,$$

and for the polarizability

$$\alpha = \frac{9}{2}; \quad \alpha = \frac{9}{2} a^3 \text{ (usual unities)} \quad (10.7)$$

□ **Contribution of continuum states**

From

$$\Delta E = \mathcal{E}^2 \sum_{n \neq 1s} \frac{|\langle 1s | z | n \rangle|^2}{E_{1s} - E_n},$$

it follows

$$\alpha = 2 \sum_{n \neq 1s} \frac{|\langle 1s | z | n \rangle|^2}{E_n - E_{1s}} \quad (10.8)$$

We see that all terms give a positive contribution to α . Angular momentum and parity conservation imply that to the sum only discrete p-states and continuum states can contribute.

It is easy to give an upper bound to α considering the lowest possible denominator: $E_{2p} - E_{1s} = 3/8$ and using completeness:

$$\alpha < \frac{2}{3/8} \sum_{n \neq 1s} |\langle 1s | z | n \rangle|^2 = \frac{16}{3} \langle 1s | z^2 | 1s \rangle = \frac{16}{3}.$$

A lower bound is obtained inserting only the $|2p; m=0\rangle$ state into the sum

$$\alpha > \frac{16}{3} |\langle 1s | z | 2p; 0 \rangle|^2.$$

The angular part of 2 p state wave function is $Y_{10}[\theta, \varphi]$ then previous angular integral is

$$\int Y_{00} Y_{10} \cos[\theta] d\Omega = \int \frac{d\Omega}{4\pi} \sqrt{3} \cos[\theta]^2 = \frac{1}{\sqrt{3}}$$

$$\alpha > \frac{16}{9} |\langle 1s || r || 2p; 0 \rangle|^2$$

where $\langle 1s || r || 2p; 0 \rangle$ stands for reduced matrix element, i.e. matrix element between radial waves functions. From

$$R_{1s} = 2 \text{Exp}[-r]; \quad R_{2p} = \frac{1}{2\sqrt{6}} r \text{Exp}[-r/2]$$

we have

$$|\langle 1s || r || 2p; 0 \rangle|^2 = \frac{2^{14}}{3^8} \frac{2}{3}; \quad \alpha > \frac{2^{19}}{3^{11}} \approx 2.95.$$

Previous computations extend immediately to all np discrete states, which are the whole discrete contribution to α :

$$\alpha_{\text{disc}} = \frac{2}{3} \sum_{n=2}^{\infty} \frac{2}{1 - \frac{1}{n^2}} |\langle 1s || r || np; 0 \rangle|^2.$$

The radial integrals can be computed,

$$|\langle 1s || r || np; 0 \rangle|^2 = 2^8 n^7 \frac{(n-1)^{2n-5}}{(n+1)^{2n+5}},$$

and the series evaluated numerically

$$\alpha_{\text{disc}} = \frac{2}{3} \sum_{n=2}^{\infty} \frac{2}{1 - \frac{1}{n^2}} 2^8 n^7 \frac{(n-1)^{2n-5}}{(n+1)^{2n+5}} \approx 3.663$$

this means that continuum contribution is

$$\alpha_c = 9/2 - \alpha_{\text{disc}} \approx 0.837.$$

We leave to the reader the following exercise : let us approximate continuous states by plane waves, show that the estimated continuum contribution will be 7/3, i.e. a bad approximation in excess of the true result.

Problem 11

Spin interactions split $n=2$ degenerate levels of hydrogen atom in two levels ($2s_{1/2}$, $2p_{1/2}$) and $2p_{3/2}$. Study the effect of an electric field (Lo Surdo-Stark effect) taking into account this separation. The level ($2s_{1/2}$, $2p_{1/2}$) is split due to radiative corrections (Lamb shift), the separation being about 10^{-6} eV. Which are the effects of this separation on the Lo Surdo-Stark effect?

● Solution

■ Orders of magnitude

In problem [7] we have studied an idealized form of Lo Surdo - Stark effect on hydrogen atom, neglecting spin effects, fine structure etc. In this problem our aim is to be more close to reality and see quantitatively the interplay of different interactions.

We remember some numbers, a.u. stands for atomic unit, Ry for Rydberg, eV for electron Volt and ΔE_{FS} for fine structure energy splitting. a is the Bohr radius:

$$1 \text{ a.u.} = 2 \text{ Ry} \approx 27.21 \text{ eV}; \quad \Delta E_{FS} \approx \alpha^2 \text{ a.u.} \approx 10^{-4} \text{ a.u.} \approx 2.7 \cdot 10^{-3} \text{ eV}; \quad a = 5.29 \cdot 10^{-9} \text{ cm.} \quad (11.1)$$

If we measure the electric field in **Volt/cm** the typical energy involved is

$$\mathcal{F} = e \mathcal{E} a \sim 5.29 \cdot 10^{-9} \text{ eV } \mathcal{E}$$

We see that up to field of the order of $10^5 - 10^6$ Volts/cm the fine structure is much bigger than electric field effects, so the previous problem was quite unrealistic for small fields.

Another energy scale is given by the separation induced by radiative corrections on $2s_{1/2}$ and $2p_{1/2}$ levels. Infrequency this separation is about 1057 MHz in energy

$$\delta E_{Lamb} \approx 1.057 \cdot 10^9 \text{ h} = 4.37 \cdot 10^{-6} \text{ eV}$$

This means that up to field of 10^3 Volts/cm this splitting is higher than electric field effects, i.e. the levels appear not degenerate. If we put real numbers for fine structure of $n=2$ level we find in effect only 1 order of magnitude between Lamb shift and fine structure, $\delta E_{Lamb} \sim 0.1 \Delta E_{FS} (n=2)$.

In real life things are complicated by the width of the states, which we neglect in this problem, and by hyperfine structure, i.e. splitting due to nuclear magnetic moment.

■ Fine structure

In this section we take into account the fine structure but neglect Lamb shift, so the solution is reasonable only for $\mathcal{E} \gg 10^3$ Volts/cm.

Level $n=2$ of hydrogen atom consists of 8 states, taking into account the spin of the electron. We know, see text, that spin orbit interaction commutes only with total angular momentum $j = L + S$. A level with a given L ($S = 1/2$ is understood for a single electron) splits according to the values of j , with $|L-S| \leq j \leq |L+S|$. Compatible quantum numbers are E, j, j_z , and in a perturbative analysis a state can be identified by $|n, L, j, j_z\rangle$, n being the principal quantum number and L the angular momentum of the unperturbed state. As we work exclusively with $n=2$ states we omit this number in the notation of states, which can be denoted by

$$|s; \frac{1}{2}, \pm \frac{1}{2}\rangle, \quad |p; \frac{1}{2}, \pm \frac{1}{2}\rangle, \quad |p; \frac{3}{2}, (\pm \frac{1}{2}, \pm \frac{3}{2})\rangle.$$

The accidental degeneracy $s - p$ survives spin orbit and relativistic corrections and $2s_{1/2}$ $2p_{1/2}$ levels remain degenerate. Radiative corrections produce an energy shift Δ_L between these two states. If we call Δ_F the fine structure splitting between $2p_{3/2}$ and $2p_{1/2}$ the energies of the levels above can be written, in order

$$E_{2p_{1/2}} + (\Delta_L, 0, \Delta_F).$$

In what follows we neglect the common energy factor and consider only splittings.

■ Selection rules

- As discussed on problem [7] the Hamiltonian in presence of an external electric field, directed along z by convention, is invariant under the reflection $\mathcal{R}: y \rightarrow -y$, or the azimuthal angle $\varphi \rightarrow -\varphi$, and this implies a degeneracy for levels with opposite j_z . In effect we discussed the symmetry only in absence of spin, but the operation \mathcal{R} can be implemented also on spinors without major changes. Even in presence of \mathcal{E} the levels have a double degeneracy and we can limit ourselves to the study of positive j_z , i.e. to four states.
- z commutes with j_z , so states with different j_z cannot mix via first order perturbation, i.e. state $|p; 2, 3/2\rangle$ is separated from other states.
- z behaves like a component of a vector, i.e. is odd under parity. This, and the previous point, imply that the only possible matrix element for $|3/2, 3/2\rangle$ (the diagonal one) vanishes. We are left with only three mixing states, $|s; 2, 3/2\rangle$, $|p; 2, 1/2\rangle$, $|p; 2, 1/2\rangle$, and for parity only $s-p$ matrix elements can be different from zero.

■ Matrix elements

We know from problem [7] that the only orbital matrix element different from zero was

$$\langle 2s | -e\epsilon z | 2p, m=0 \rangle = 3e\epsilon a. \tag{11.2}$$

to compute the full matrix of perturbation we have only to write decomposition of states into orbital and spinpart, i.e. use Clebsch-Gordan coefficients. Denoting by ψ_{lm} the orbital part of the state and by $|\uparrow\rangle$ and $|\downarrow\rangle$ the spinors, we have

$$\begin{aligned} |p; \frac{1}{2}, \frac{1}{2}\rangle &= \sqrt{\frac{2}{3}} \psi_{2p,1} |-\rangle - \sqrt{\frac{1}{3}} \psi_{2p,0} |+\rangle; \\ |p; \frac{1}{2}, \frac{1}{2}\rangle &= \sqrt{\frac{1}{3}} \psi_{2p,1} |-\rangle + \sqrt{\frac{2}{3}} \psi_{2p,0} |+\rangle; \quad |s; \frac{1}{2}, \frac{1}{2}\rangle = \psi_{2s,0} |+\rangle; \end{aligned}$$

Using (2) matrix elements for the perturbation, both Stark and Hyperfine splitting, are given by (the order of rows is the one in which states are written in previous equation):

$$V = \begin{pmatrix} \Delta_F & 0 & -\sqrt{2}x \\ 0 & 0 & x \\ -\sqrt{2}x & x & \Delta_L \end{pmatrix}; \quad \text{where } x \equiv \sqrt{3} e\epsilon a. \tag{11.3}$$

Solutions of the secular equation $\det(V-\lambda) = 0$, gives energy levels.

Let us now consider different regimes

□ $x \gg \Delta_F \gg \Delta_L$ (i.e. $\epsilon \gg 10^9$ v / cm)

In this regime approximatively we have to solve

$$\det \begin{pmatrix} -\lambda & 0 & -\sqrt{2}x \\ 0 & -\lambda & x \\ -\sqrt{2}x & x & -\lambda \end{pmatrix} = 0 \Rightarrow -\lambda^3 + 3x^2\lambda = 0; \Rightarrow \lambda = \left(0, \pm\sqrt{3}x\right) = (0, \pm 3e\epsilon a) \tag{11.4}$$

We recover the result of problem [7]. Remembering the decoupled and unaffected $|p;3/2,3/2\rangle$ state and the doubling $j_z \rightarrow -j_z$ we have 4 states at energy 0, 2 states at energy $3e\epsilon a$ and 2 states at energy $-(3e\epsilon a)$. The doubling in the degeneracy with respect to problem [7] is due to spin. We have as expected a linear Stark effect.

□ $x \ll \Delta_L \ll \Delta_F$ (i.e. $\epsilon \ll 10^3$ v / cm)

It is a useful exercise to compute approximate eigenvalues of (3) using perturbation theory to this matrix, x - terms elements are the perturbation, δV . There are no diagonal elements, so first order effect is zero, and correction start from x^2 . At second order consider for example the first state. We have as is well known

$$\Delta E_1 = \langle 1 | \delta V | n \rangle \frac{1}{E_1 - E_n} \langle n | \delta V | 1 \rangle = \langle 1 | \delta V | 3 \rangle \frac{1}{E_1 - E_3} \langle 3 | \delta V | 1 \rangle = \frac{2x^2}{\Delta_F - \Delta_L}; \quad E_1 = \Delta_F + \Delta E_1 \tag{11.5}$$

For the other two levels we have respectively

$$\Delta E_2 = -\frac{x^2}{\Delta_L}; \quad \Delta E_3 = x^2 \left(\frac{1}{\Delta_L} - \frac{2}{\Delta_F - \Delta_L} \right); \quad E_3 = \Delta_L + \Delta E_3.$$

□ $\Delta_L \ll x \ll \Delta_F$

This case is a bit academic as for n=2 levels $\Delta_L \sim 0.1 \Delta_F$ but can be a useful exercize for the reader. Neglecting Δ_L the matrix (3) becomes

$$V = \begin{pmatrix} \Delta_F & 0 & -\sqrt{2}x \\ 0 & 0 & x \\ -\sqrt{2}x & x & 0 \end{pmatrix}; \tag{11.6}$$

The last two states, $|p;1/2,1/2\rangle$ and $|s;1/2,1/2\rangle$ are degenerate and we have to apply for the submatrix 2x2 degenerate perturbation theory. Eigenstates and eigenvalues are obvious

$$|A\rangle = \frac{1}{\sqrt{2}} (|2\rangle + |3\rangle); \quad \text{eig. } +x; \quad |B\rangle = \frac{1}{\sqrt{2}} (|2\rangle - |3\rangle); \quad \text{eig. } -x.$$

In the new basis, $|1\rangle, |A\rangle, |B\rangle$ the matrix V reads

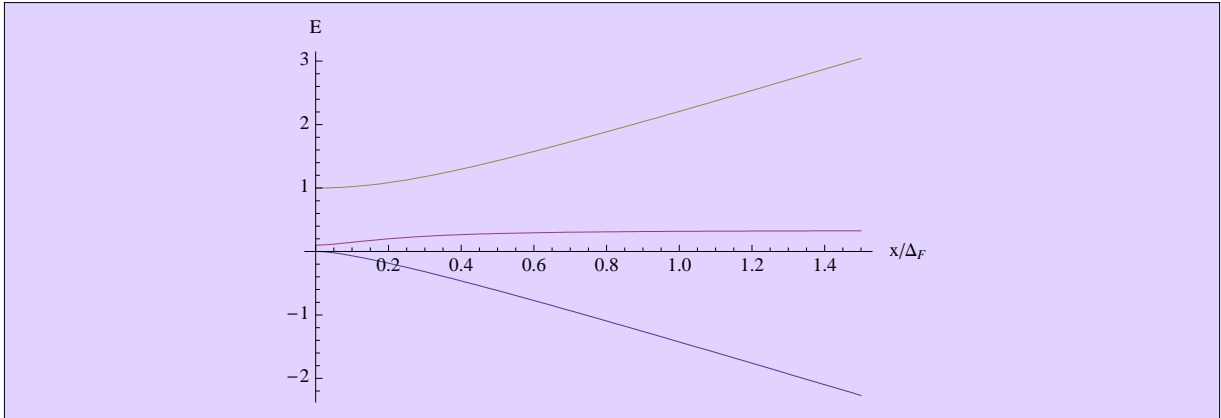
$$V = \begin{pmatrix} \Delta_F & -x & x \\ -x & x & 0 \\ x & 0 & -x \end{pmatrix}.$$

Now we can apply non degenerate perturbation theory to first state, i.e. formula (5) obtaining

$$E_1 = \Delta_F + 2 \frac{x^2}{\Delta_F}.$$

Then, as expected, the two degenerate states $|p;1/2,1/2\rangle$, $|s;1/2,1/2\rangle$ have a linear Stark effect, while the third state, here $|p;3/2,1/2\rangle$ has a quadratic Stark effect.

In the figure below we present energy levels as a function of x / Δ_F , with $\Delta_L = 0.1 \Delta_F$. We note that linear Stark effect is quite precocious and start at about $x / \Delta_F \sim 0.6$.



A useful exercise that we leave for the reader is to consider Stark effect as the leading term and fine structure as a perturbation, i.e. compute higher orders in (4).

Problem 12

Parabolic coordinates (ξ, η, φ) are defined by

$$x = \sqrt{\xi \eta} \cos[\varphi]; \quad y = \sqrt{\xi \eta} \sin[\varphi]; \quad z = \frac{1}{2} (\xi - \eta);$$

In notebook problems [*] it has been shown that Schrödinger equation for an hydrogen atom is separable in these coordinates. Study the Lo Surdo - Stark effect in parabolic coordinates. Compute first and second order effects for an arbitrary state.

● Solution

■ The Schrödinger equation

In this notebook we will use *atomic units*, $\hbar = m = |e| = 1$.

In notebook [*] the results obtained here are derived within *Mathematica* and extended to an arbitrary order in perturbation theory.

In notebook [*] the Schrödinger equation for a coulombic potential has been solved in parabolic coordinates. We report here the basic connection formulae between cartesian and parabolic coordinates and the for of the laplacian:

$$\begin{aligned} x &= \sqrt{\xi \eta} \cos[\varphi]; \quad y = \sqrt{\xi \eta} \sin[\varphi]; \quad z = \frac{1}{2} (\xi - \eta); \\ \xi &= r + z; \quad \eta = r - z; \quad \varphi = \text{ArcTan}\left[\frac{y}{x}\right]; \quad r = \frac{1}{2} (\xi + \eta); \\ \Delta &= \frac{4}{\xi + \eta} \frac{\partial}{\partial \xi} \left(\xi \frac{\partial}{\partial \xi} \right) + \frac{4}{\xi + \eta} \frac{\partial}{\partial \eta} \left(\eta \frac{\partial}{\partial \eta} \right) + \frac{1}{\xi \eta} \frac{\partial^2}{\partial \varphi^2}. \end{aligned} \quad (12.1)$$

The range for these coordinates is

$$0 \leq (\xi, \eta) \leq \infty; \quad 0 \leq \varphi \leq 2\pi$$

and volume element is

$$d^3 \mathbf{x} = \frac{\xi + \eta}{4} d\xi d\eta d\varphi.$$

Interaction with an electric field \mathcal{E} , directed along z by convention, is described by an interaction $-e z \mathcal{E} = +|e| z \mathcal{E}$. We put F for the product $|e| \mathcal{E}$ in atomic units (a is the Bohr radius) and write the interaction Hamiltonian as (see eq. (1))

$$V = \frac{F}{2} (\xi - \eta). \quad (12.2)$$

Using (1) the Schrödinger equation takes the form:

$$-\frac{1}{2} \left(\frac{4}{\xi + \eta} \frac{\partial}{\partial \xi} \left(\xi \frac{\partial}{\partial \xi} \right) + \frac{4}{\xi + \eta} \frac{\partial}{\partial \eta} \left(\eta \frac{\partial}{\partial \eta} \right) + \frac{1}{\xi \eta} \frac{\partial^2}{\partial \varphi^2} \right) \psi - \frac{2Z}{\xi + \eta} \psi + \frac{F}{2} (\xi - \eta) \psi = E \psi.$$

or

$$\left(\frac{\partial}{\partial \xi} \left(\xi \frac{\partial}{\partial \xi} \right) + \frac{\partial}{\partial \eta} \left(\eta \frac{\partial}{\partial \eta} \right) + \frac{\xi + \eta}{4 \xi \eta} \frac{\partial^2}{\partial \varphi^2} \right) \psi + \left(Z - \frac{F}{4} (\xi^2 - \eta^2) + \frac{\xi + \eta}{2} E \right) \psi = 0. \quad (12.3)$$

The system is invariant under rotation around z axis, then one of the "good" quantum numbers will be m, the eigenvalue of L_z . We look for a solution with separate variables, in the form

$$\psi = f_1[\xi] f_2[\eta] \text{Exp}[i m \varphi]. \quad (12.4)$$

Substitution in (3), after division by ψ , gives

$$\frac{1}{f_1} \left(\frac{d}{d\xi} \left(\xi \frac{df_1}{d\xi} \right) - \frac{m^2}{4\xi} f_1 + \frac{E}{2} \xi f_1 - \frac{F}{4} \xi^2 f_1 \right) + \frac{1}{f_2} \left(\frac{d}{d\eta} \left(\eta \frac{df_2}{d\eta} \right) - \frac{m^2}{4\eta} f_2 + \frac{E}{2} \eta f_2 + \frac{F}{4} \eta^2 f_2 \right) + Z = 0.$$

The first term depends only on ξ , the second only on η , since their sum is constant there must be two constant Z_1 and Z_2 such that

$$\begin{aligned} \frac{d}{d\xi} \left(\xi \frac{df_1}{d\xi} \right) + \left(\frac{E}{2} \xi - \frac{m^2}{4\xi} - \frac{F}{4} \xi^2 + Z_1 \right) f_1 &= 0; \\ \frac{d}{d\eta} \left(\eta \frac{df_2}{d\eta} \right) + \left(\frac{E}{2} \eta - \frac{m^2}{4\eta} + \frac{F}{4} \eta^2 + Z_2 \right) f_2 &= 0; \\ Z_1 + Z_2 &= Z. \end{aligned} \quad (12.5)$$

We can simplify a bit these equations by the change of variables

$$\epsilon = \sqrt{-2E}; \quad x = \epsilon \xi; \quad y = \epsilon \eta; \quad \beta_i = \frac{Z_i}{\epsilon}; \quad \mathcal{F} = \frac{F}{\epsilon^3}. \quad (12.6)$$

$$\begin{aligned} \frac{d}{dx} \left(x \frac{df_1}{dx} \right) + \left(-\frac{1}{4} x - \frac{m^2}{4x} - \frac{\mathcal{F}}{4} x^2 + \beta_1 \right) f_1 &= 0; \\ \frac{d}{dy} \left(y \frac{df_2}{dy} \right) + \left(-\frac{1}{4} y - \frac{m^2}{4y} + \frac{\mathcal{F}}{4} y^2 + \beta_2 \right) f_2 &= 0; \\ \beta_1 + \beta_2 &= \frac{Z}{\epsilon}. \end{aligned} \quad (12.7)$$

As is apparent from (7) the spectrum depends only on $|m|$, and, as we know from general arguments, states $\pm m$ will be degenerate.

The procedure to find eigenvalues, as in the case $\mathcal{E} = 0$, is the following

1. Find, for each \mathcal{F} , eigenvalues β_1, β_2 , these will depend parametrically on \mathcal{F} .
2. Substitute in the last constraint in (7) and find ϵ (i.e. energy) as a function of \mathcal{F} .

■ **Perturbative solution at first order**

At zero order the solution of equations (7) has been found in notebook [*]. Normalizability of the solutions impose

$$\beta_1 = n_1 + \frac{|m| + 1}{2}; \quad \beta_2 = n_2 + \frac{|m| + 1}{2}; \quad \Rightarrow \quad \beta_1 + \beta_2 = n_1 + n_2 + (|m| + 1) \equiv n; \quad (12.8)$$

then

$$\beta_1 + \beta_2 = \frac{Z}{\epsilon} \quad \Rightarrow \quad \epsilon = \frac{Z}{n} \quad \Rightarrow \quad E = -\frac{1}{2n^2} \quad (12.9)$$

At fixed n, $0 \leq |m| \leq n-1$ and with fixed n and m, one of the two numbers, e.g. n_1 , can vary as $0 \leq n_1 \leq n - |m| - 1$, the other being fixed by (8).

Normalized eigenfunctions are given by

$$f_{n_1, m}[x] = \sqrt{\frac{n!}{(n+|m|)!}} x^{|m|/2} \text{Exp}\left[-\frac{x}{2}\right] L_n^{|m|}(x) \equiv c_{n_1, m} x^{|m|/2} \text{Exp}\left[-\frac{x}{2}\right] L_n^{|m|}(x)$$

$$\int_0^\infty f_{n_1, m} f_{n_2, m} dx = \delta_{n_1 n_2}.$$

We will comment below on the normalization coefficients.

The perturbative calculation is done *independently* on the two equations in (7), each of them is a kind of Schrödinger equation in which β_1 has the role of energy eigenvalue. It is sufficient to do computations for β_1 , the other one is obtained by $\mathcal{F} \rightarrow -\mathcal{F}$.

To compute perturbative corrections we need matrix elements of x^2 . We start from recursive relation

$$x L_n^m(x) = -(n+m) L_{n-1}^m(x) - (n+1) L_{n+1}^m(x) + (2n+m+1) L_n^m(x). \quad (12.11)$$

Denoting the diagonal matrix element by $\langle f_n | x^2 | f_n \rangle$, using (11) to right and left functions, and inserting normalization coefficients, we have immediately (by orthogonality and omitting the fixed index m):

$$\langle f_n | x^2 | f_n \rangle = \frac{c_n^2}{c_{n+1}^2} (n+1)^2 + \frac{c_n^2}{c_{n-1}^2} (n+m)^2 + (2n+m+1) = 6n^2 + 6n(m+1) + (m+1)(m+2). \quad (12.12)$$

Up to first order then

$$\beta_1 = n_1 + \frac{|m|+1}{2} + \frac{\mathcal{F}}{4} (6n_1^2 + 6n_1(m+1) + (m+1)(m+2));$$

$$\beta_2 = n_2 + \frac{|m|+1}{2} + \frac{\mathcal{F}}{4} (6n_2^2 + 6n_2(m+1) + (m+1)(m+2)).$$

and, see the definition of n in (8):

$$\beta_1 + \beta_2 = n + \mathcal{F} \left(\frac{3}{2} (n_1^2 - n_2^2) + \frac{3}{2} (n_1 - n_2)(m+1) \right) = n + \frac{3}{2} \mathcal{F} (n_1 - n_2) n. \quad (12.13)$$

Imposing the constraint (7), using $\mathcal{F} = F/\epsilon^3$ and the zeroth order result $\epsilon = Z/n$

$$\frac{Z}{\epsilon} = n + \frac{3}{2} \frac{F}{\epsilon^3} (n_1 - n_2) n \approx n + \frac{3}{2} \frac{F}{Z^3} (n_1 - n_2) n^4 \Rightarrow$$

$$\frac{\epsilon}{Z} \approx \frac{1}{n} \left(1 - \frac{3}{2} \frac{F}{Z^3} (n_1 - n_2) n^3 \right) \Rightarrow \epsilon \approx \frac{Z}{n} - \frac{3}{2} F \left(\frac{n}{Z} \right)^2 (n_1 - n_2),$$

and finally for energy, $E = -\epsilon^2/2$

$$E = -\frac{1}{2} \frac{Z^2}{n^2} + \frac{3}{2} F \frac{n}{Z} (n_1 - n_2). \quad (12.14)$$

This gives the first order Stark effect on all levels. It is easy to check low level to compare with more elementary results (prob. [7]), we consider hydrogen, $Z=1$:

$$n=1; m=0; (n_1, n_2) = 0 \Rightarrow \delta E = 0;$$

$$n=2; m=0; (n_1, n_2) = (1, 0), (0, 1) \Rightarrow \delta E = \mp 3 F;$$

$$n=2; m=\pm 1; (n_1, n_2) = (0, 0), (0, 1) \Rightarrow \delta E = 0;$$

We have the known Stark effect on level $n=2$, to compare with problem [7] use $F = e \mathcal{E} a$.

□ The normalization of wave functions

The eigenfunctions (10) are a *complete* and *orthonormal* set with respect the measure dx . The eigenfunctions used in notebook [*] where similar but not identical. In ξ variable they were

$$\psi_{n_1 n_2 m}[\xi, \eta, \varphi] := f_{n_1 m}[\xi] f_{n_2 m}[\eta] \frac{e^{i m \varphi}}{\sqrt{2\pi}};$$

$$f_{n_1 m}[\xi] = 2^{1/4} \epsilon \sqrt{\frac{n!}{(n+|m|)!}} (\epsilon \xi)^{|m|/2} e^{-\epsilon \xi/2} L_n^{|m|}(\epsilon \xi) \quad (12.15)$$

Functions (15) are orthogonal with respect the three dimensional measure induced by parabolic coordinates, i.e.

$$\int \psi_{n_1 n_2 m}^* \psi_{k_1 k_2 m} \frac{\xi + \eta}{4} d\xi d\eta d\varphi = \delta_{n_1 k_1} \delta_{n_2 k_2} \delta_{m m}$$

Functions (15) are not a complete set with respect to this measure, we clearly miss continuum spectrum. In this problem eigenfunctions (10) are used to solve the auxiliary problem (7). For negative energies we look at real eigenvalues β_i and in this framework (at $\mathcal{F} = 0$) functions (10) are a complete set. If we make the change of variables

$$f[\mathbf{x}] = \mathbf{x}^{-1/2} g[\mathbf{x}]$$

the first equation (7) becomes

$$\frac{d^2}{dx^2} g[\mathbf{x}] + \left(\frac{1}{4x^2} - \frac{1}{4}x - \frac{m^2}{4x} - \frac{\mathcal{F}}{4}x^2 + \beta_1 \right) g[\mathbf{x}],$$

i.e. a "usual" one dimensional Schrödinger equation with potential

$$2V[\mathbf{x}] = \frac{1}{4}x + \frac{m^2}{4x} - \frac{1}{4x^2} + \frac{\mathcal{F}}{4}x^2$$

and have only a bound spectrum for $\mathcal{F} = 0$. For $\mathcal{F} = 0$ both equations (7) admit only a discrete spectrum, the continuous spectrum of the coulomb potential comes from $E > 0$ and ϵ imaginary. The constraint in this case force to look for imaginary eigenvalues.

When $\mathcal{F} \neq 0$ one of the two equations has a potential non bounded below at infinity, for example the second one if $\mathcal{F} > 0$, the energy levels will be instable for tunneling, this phenomenon will be analysed with WKB methods, but do not concerne us as far as we consider perturbation theory.

■ **Perturbative solution at second (and third) order**

It is not difficult extend the solution to second order, First we write implicitly the correction $\psi^{(1)}$ to wave functions in the two eigenvalue problems (7)

$$\psi_n^{(1)}[\mathbf{x}] = \sum_s' f_s[\mathbf{x}] \frac{\langle f_s | V | f_n \rangle}{\beta_n - \beta_s}; \quad V = \frac{\mathcal{F}}{4}x^2; \tag{12.16}$$

then we use the general formulae

$$\delta E_n^{(2)} = \langle \psi_0 | V | \psi_n^{(1)} \rangle, \quad \delta E_n^{(3)} = \langle \psi_n^{(1)} | V | \psi_n^{(1)} \rangle - \delta E_n^{(1)} \langle \psi_n^{(1)} | \psi_n^{(1)} \rangle. \tag{12.17}$$

Iterating recursion relation (11) we obtain

$$x^2 L_n^m = (n+2)(n+1)L_{n-2}^m - 2(n+1)(2n+m+2)L_{n-1}^m + (6n(n+m+1) + (m+2)(m+1))L_n^m - 2(n+m)(m+2)L_{n+1}^m + (m+n)(n+m-1)L_{n+2}^m. \tag{12.18}$$

Let us call d_k ($k = -2, \dots, +2$) the coefficients of this relation. Using normalization constants c_k this relation can be transformed in a recursive relation for basis functions:

$$x^2 f_k[\mathbf{x}] = \sum_{k=-2}^2 \frac{c_n}{c_{n+k}} d_k f_{n+k}[\mathbf{x}]. \tag{12.19}$$

Using orthogonality of basis functions the first order correction (16) is

$$\psi_n^{(1)}[\mathbf{x}] = \frac{\mathcal{F}}{4} \sum_{k=-2, k \neq 0}^2 \frac{1}{\beta_n^{(0)} - \beta_{n+k}^{(0)}} \frac{c_n}{c_{n+k}} d_k f_{n+k}[\mathbf{x}] \tag{12.20}$$

Now we have only to insert (20) in (17) and using (12) and orthogonality to perform integrals. The result with $\mathcal{F} \rightarrow -\mathcal{F}$ will give correction to β_2 .

Imposing the constraint (7) will give the corrections to energy levels. We report here the final result of this straightforward but tedious computation

$$E = -\frac{Z^2}{2n^2} + \frac{3}{2}F \frac{n}{Z} (n_1 - n_2) - \frac{1}{16}F^2 \left(\frac{n}{Z}\right)^4 [17n^2 - 3(n_1 - n_2)^2 - 9m^2 + 19] + \frac{3}{32}F^3 \left(\frac{n}{Z}\right)^7 (n_1 - n_2) [23n^2 - (n_1 - n_2)^2 + 11m^2 + 39]. \tag{12.21}$$

A method to perform the computation to all orders is given in notebook [**]. in particular for the ground state of hydrogenic atoms ($n=1, n_1 = n_2 = 0, m = 0$) one obtains

$$E = -\frac{Z^2}{2n^2} - \frac{9}{4}F^2 \frac{1}{Z^4}.$$

From previous result the polarizability α follows

$$\alpha F = - \frac{\partial E}{\partial F} = \frac{9}{2} \frac{F}{Z^4}$$

which reproduces the known result of hydrogen atom, see problem[**].

Problem 13

Consider electron - electron interaction as a small perturbation in an helium atom. Compute to lowest order the energy of ground state of helium atom. Compute 3-dimensional Fourier transform for the functions

$$\frac{1}{r}; \quad \frac{\text{Exp}[-\mu r]}{r}; \quad \text{Exp}[-\mu r];$$

and show how these results can be used to solve the problem.

● Solution

■ Introduction

This problem is intended as an introduction to the next one, prob.[14].

In this problem we will use atomic units. Units for length and energy are

$$a_B = \frac{\hbar^2}{m e^2} \quad (\text{Bohr radius}); \quad E_B = \frac{m e^4}{\hbar^2} = \frac{e^2}{a_B} \approx 27.2114 \text{ eV} \quad (13.1)$$

In these units the non relativistic Hamiltonian for Helium atom is

$$H = - \frac{1}{2} \Delta_1 - \frac{1}{2} \Delta_2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \equiv H_0 + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (13.2)$$

Suffixes 1,2 refer to the electrons. $\mathbf{r}_1, \mathbf{r}_2$ are their position with respect to nucleus, $r_1 = |\mathbf{r}_1|$ etc. Z is the nuclear charge, Z = 2 for helium otherwise we will describe ions of Berillium, Z=3, Boron, Z=4 etc.

In this problem we are considering electron-electron interaction as a perturbation. We do not expect good quantitative results as its order of magnitude, e^2/a_B in usual units, is similar to other terms in the Hamiltonian.

H_0 is a sum of independent hamiltonians, then its ground state is written at once

$$\Psi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{1s}(\mathbf{r}_1) \psi_{1s}(\mathbf{r}_2); \quad E_0 = E_{1s} + E_{1s} = - \frac{Z^2}{2} \left(\frac{1}{1} + \frac{1}{1} \right) = -Z^2. \quad (13.3)$$

■ Perturbation

The perturbative contribution to the energy of the ground state is

$$\Delta E = \langle 1s; 1s | \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} | 1s; 1s \rangle = \int d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 \frac{|\psi_{1s}(\mathbf{r}_1)|^2 |\psi_{1s}(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (13.4)$$

The most simple and general way to compute integrals like (4) is to use *multipole expansion* for Coulomb potential:

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{\ell=0}^{\infty} \frac{1}{r_>} \left(\frac{r_<}{r_>} \right)^{\ell} P_{\ell}[\text{Cos}(\gamma)]; \quad (13.5)$$

with P_{ℓ} Legendre polynomials and

$$r_> = \text{Max}[r_1, r_2]; \quad r_< = \text{Min}[r_1, r_2]; \quad \mathbf{r}_1 \cdot \mathbf{r}_2 = r_1 r_2 \text{Cos}[\gamma].$$

In the actual case our distribution are spherically symmetric, only $\ell=0$ term in the sum survives angular integration and we have, splitting the integral:

$$\begin{aligned} \Delta E &= \int d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 \rho(\mathbf{r}_1) \frac{1}{r_>} \rho(\mathbf{r}_2) = \\ (4\pi)^2 \left(\int_0^{\infty} d r_1 r_1^2 \rho(r_1) \frac{1}{r_1} \int_0^{r_1} \rho(r_2) r_2^2 d r_2 + \int_0^{\infty} d r_2 r_2^2 \rho(r_2) \frac{1}{r_2} \int_0^{r_2} \rho(r_1) r_1^2 d r_1 \right) = \\ &2 (4\pi)^2 \int_0^{\infty} d r_1 r_1^2 \rho(r_1) \frac{1}{r_1} \int_0^{r_1} \rho(r_2) r_2^2 d r_2. \end{aligned} \quad (13.6)$$

Using the known wave functions

$$\psi_{1s} = Y_{00} R_{1s}[r] = \frac{1}{\sqrt{4\pi}} 2 Z^{3/2} \text{Exp}[-Zr].$$

it is easy to compute

$$\Delta E = 2 \times \frac{5}{16} Z = \frac{5}{8} Z. \tag{13.7}$$

For the energy the prediction is (for $Z = 2$)

$$E = -Z^2 + \frac{5}{8} Z \rightarrow -2.75 \text{ a.u.}; \quad E_{\text{exp}} \approx -2.90 \text{ a.u.}$$

Usually what is reported is ionization energy, i.e. the energy necessary to extract one electron. After ionization we have a one electron atom, with energy $-Z^2/2$ then ionization energy is defined as (we neglect relativistic corrections)

$$I = -\frac{Z^2}{2} - E_0 \approx \frac{Z^2}{2} - \frac{5}{8} Z = 0.75 \text{ a.u.} = 1.5 \text{ Ry} = 20.41 \text{ eV.}$$

to be compared with

$$I_{\text{exp}} \approx 0.9035 \text{ a.u.} = 1.807 \text{ Ry} = 24.5855 \text{ eV.}$$

■ **Different methods to compute an integral**

The multipole expansion (5) is a standard way to compute integrals of the form (4), nevertheless it can be useful to have alternative strings in one's bow.

□ **Electrostatic analogy**

The integral (4) is the double of an electrostatic self-energy for a charge density ρ :

$$\Delta E = 2U; \quad U = \frac{1}{2} \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

Let us divide the space in shells of width dr , with charge $\rho(r) 4\pi r^2 dr$. The self energy can be obtained by summing potential energy of these shells, the potential being created by charge inside sphere of radius r . The total charge up to radius r , $Q(r)$ creates a potential $Q(r)/r$ at limiting radius r , hence the self energy is

$$U = \int_0^\infty 4\pi r^2 dr \rho(r) \frac{1}{r} Q(r)$$

Once multiplied by the additional factor of two this expression coincides with (6).

□ **Fourier transforms**

In this book, as often in Physics literature, the Fourier transforms are defined in an asymmetric way:

$$f[\mathbf{x}] = \int \frac{d^n \mathbf{k}}{(2\pi)^n} \mathcal{F}_f[\mathbf{k}] e^{i\mathbf{k}\cdot\mathbf{x}}; \quad \mathcal{F}_f[\mathbf{k}] = \int d^n \mathbf{x} \mathcal{F}_f[\mathbf{k}] e^{-i\mathbf{k}\cdot\mathbf{x}}. \tag{13.8}$$

This method is based on two well known facts about Fourier transforms :

$$\int d^n \mathbf{x} f^*[\mathbf{x}] g[\mathbf{x}] = \int \frac{d^n \mathbf{k}}{(2\pi)^n} \mathcal{F}_f^*[\mathbf{k}] \mathcal{F}_g[\mathbf{k}]; \quad \mathcal{F}_{f*g}[\mathbf{k}] = \mathcal{F}_f[\mathbf{k}] \mathcal{F}_g[\mathbf{k}]. \tag{13.9}$$

For real functions $\mathcal{F}_f^*[\mathbf{k}] = \mathcal{F}_f[-\mathbf{k}]$. $f*g$ is the convolution of two functions, i.e.

$$f * g[\mathbf{x}] = \int d^n \mathbf{y} f[\mathbf{x} - \mathbf{y}] g[\mathbf{y}].$$

Direct application of (9) gives for the integral (4):

$$\Delta E = \int \frac{d^n \mathbf{k}}{(2\pi)^n} \mathcal{F}_\rho^*[\mathbf{k}] \mathcal{F}_{1/r}[\mathbf{k}] \mathcal{F}_\rho[\mathbf{k}]. \tag{13.10}$$

By direct computation, or by taking the Fourier transforms of the equations

$$-\Delta \frac{1}{r} = 4\pi \delta^{(3)}(\mathbf{r}); \quad (-\Delta + \mu^2) \frac{e^{-\mu r}}{r} = 4\pi \delta^{(3)}(\mathbf{r});$$

we have

$$\mathcal{F}_{1/r}[\mathbf{k}] = \frac{4\pi}{k^2}; \quad \mathcal{F}\left[\frac{e^{-\mu r}}{r}\right][\mathbf{k}] = \frac{4\pi}{k^2 + \mu^2}.$$

From the second of these relations follows

$$\mathcal{F}[e^{-\mu r}][\mathbf{k}] = -\frac{\partial}{\partial \mu} \mathcal{F}\left[\frac{e^{-\mu r}}{r}\right][\mathbf{k}] = \frac{8\pi\mu}{(k^2 + \mu^2)^2}.$$

In our computation :

$$\rho = |\psi_{1s}|^2 = \frac{Z^3}{\pi} \text{Exp}[-2Zr]; \quad \mathcal{F}_\rho[\mathbf{k}] = 16 \frac{Z^4}{(k^2 + 4Z^2)^2};$$

and

$$\Delta E = \frac{16^2}{(2\pi)^3} 4\pi \int d^3k \frac{Z^8}{(k^2 + 4Z^2)^4} \frac{1}{k^2} = \frac{2 \cdot 16^2}{\pi} \int_0^\infty \frac{Z^8}{(k^2 + 4Z^2)^4} dk = \frac{4}{\pi} Z \int_0^\infty \frac{1}{(x^2 + 1)^4} dx = \frac{5}{8} Z$$

The last integral can be computed by method of residues. This use of Fourier transforms may seem complicated but the reader must note that it automatically transform a doubleintegral like (4) in a simple integral, like the one just computed.

Problem 14

Let us consider electron - electron interaction as a small perturbation in an helium atom. Compute at lowest order the energy of first excited s state of helium atom. Discuss how Pauli principle select possible states.

● Solution

■ Introduction

In this notebook we will use atomic units. Units for length and energy are

$$a_B = \frac{\hbar^2}{m e^2} \text{ (Bohr radius); } \quad E_B = \frac{m e^4}{\hbar^2} = \frac{e^2}{a_B} \approx 27.2114 \text{ eV} \quad (14.1)$$

In these units the non relativistic Hamiltonian for Helium atom is

$$H = -\frac{1}{2} \Delta_1 - \frac{1}{2} \Delta_2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \equiv H_0 + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (14.2)$$

Suffixes 1,2 refer to the electrons. $\mathbf{r}_1, \mathbf{r}_2$ are their position with respect to nucleus, $r_1 = |\mathbf{r}_1|$ etc. Z is the nuclear charge, Z=2 for helium otherwise we will describe ions of Berillium, Z=3, Boron, Z=4 etc.

In this problem we are considering electron-electron interaction as a perturbation. We do not expect good quantitative results as its order of magnitude, e^2/a_B in usual units, is similar to other terms in the Hamiltonian, but the perturbative computations will give us some hints on the general properties of the spectrum.

□ Quantum numbers

We are neglecting spin interactions, albeit as we will see spin enter in the determination of energies. Hamiltonian (2) is invariant under global rotations, i.e. \mathbf{L} and L_z are conserved. \mathbf{L} is total angular momentum:

$$\mathbf{L} = \boldsymbol{\ell}_1 + \boldsymbol{\ell}_2. \quad (14.3)$$

Energy in general will depend on L, and, always neglecting spin and other effects (as Pauli principle) we expect at least a degeneracy $2L+1$ for each level. To know how levels are organized we need more dynamical information, this is why we use perturbation theory.

Hamiltonian H_0 has a much bigger symmetry, it is symmetric under independent rotations of first and second electron. Each rotation invariance imply a degeneracy $(2\ell+1)$ then for H_0 we have at least a degeneracy $(2\ell_1 + 1)(2\ell_2 + 1)$. In effect we have more degeneracy as H_0 is symmetric under the exchange of the two electrons, then given a state with quantum numbers (a,b) (and a b) then the state (b,a) will have the same energy. Finally H_0 is of coulomb type and the accidental degeneracy typical of hydrogen-like systems is at work, i.e. energies depend only on principal quantum number and not on ℓ , this will be a minor complication.

H_0 is a sum of independent hamiltonians then eigenstates and energies are written at once:

$$\Psi_{ab}(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2); \quad E_{a,b} = E_a + E_b = -\frac{Z^2}{2} \left(\frac{1}{n_a^2} + \frac{1}{n_b^2} \right). \quad (14.4)$$

ψ_a, ψ_b are one electron states in coulomb potential and a,b the relative quantum numbers, i.e. n, l, m.

□ **Pauli principle**

Taking into account the overall spin degeneracy, 4 spin states, and neglecting the accidental coulombic degeneracy, on the basis of (4) we have the following list of levels. We write individual quantum numbers of the electrons to select the level, and write possible total angular momentum and spin using the known rules for summing angular momenta:

State	deg.	(L, S)	(L, S) observed
(1 s, 1 s)	4	(0, 0), (0, 1)	(0, 0) deg. 1
(1 s, 2 s) or (2 s, 1 s)	$4 \times 2 = 8$	2 (0, 0), 2 (0, 1)	(0, 0) deg. 1 (0, 1) deg. 3 4 states
(1 s, 2 p) or (2 p, 1 s)	$2 \times 4 \times 3 = 24$	$2 \times (1, 0), 2 (1, 1)$	(1, 0) deg. 3 (1, 1) deg. 9 12 states

We see that the observed states are half of the predicted ones, this is a consequence of Pauli principle, or in general of the antisymmetry of total wave function. Each function of two variables can always be decomposed in a symmetric and one antisymmetric part: Spin Statistics theorem imply that **only** antisymmetric states are physical states, and this explain the halving of states. We want to stress some points:

- Functions $\Psi_{a,b}$ and $\Psi_{b,a}$ are *different* functions, as an example

$$\psi_{1s}[\mathbf{r}_1] \psi_{2s}[\mathbf{r}_2] \neq \psi_{1s}[\mathbf{r}_2] \psi_{2s}[\mathbf{r}_1]$$

they are even orthogonal!. This is why the factor 2 due to symmetry exchange $1 \leftrightarrow 2$ appears in the degeneracy.

- Last column levels are those permitted by statistics, symmetry of spin function will force the symmetry of the corresponding orbital function, so to a symmetric S=1 spin state will correspond an antisymmetric orbital function, while to an antisymmetric S=0 spin state will correspond a symmetric orbital wave function.
- Statistics explain the total number of states, do not explain the splitting implicitly exposed in the last column. In effect it is safe to say that if two level *can* split they *will* split, due to a perturbation. It is important that the reader appreciate that in this problem (and for a general atom) the perturbation is the electrostatic repulsion between electron, *which has nothing to do with spin*. Then while statistics (and hence spin) is responsible for the halving of the states, their actual splitting is of electrostatic origin, then quite large on an atomic scale.
- We have classified the final levels with (L,S) which are good quantum numbers of the whole Hamiltonian, not simply of H_0 , then this is a good classification, and could be changed only if we add some more terms to H.

■ **Energy of excited s - states**

Helium states can be classified according to their total spin, S=0 states constitute the *parahelium* spectrum, S=1 the *orthoHelium* spectrum. S=0 and S=1 are respectively antisymmetric and symmetric in spin. The opposite symmetry must be own by the orbital part of the wave function. We note that symmetry can be read at lowest order in perturbation theory, being the perturbation symmetric, higher order corrections do not change symmetry properties.

□ **1s1s \equiv 1 s² state**

At lowest order in perturbation theory its wave function is necessarily symmetric, being the product of the same single orbital wave function:

$$\Psi_{1s1s}(\mathbf{r}_1, \mathbf{r}_2) = \psi_{1s}(\mathbf{r}_1) \psi_{1s}(\mathbf{r}_2)$$

This means that Pauli principle imply S=0 for the spinpart, i.e. the ground state is a parahelium state.

□ **1s2s state**

This is the first excited state. Spin statistics theorem imply

$$\begin{aligned} S = 0 & \quad \Psi_{1s2s}(\mathbf{r}_1, \mathbf{r}_2) \text{ antisymmetric} \\ S = 1 & \quad \Psi_{1s2s}(\mathbf{r}_1, \mathbf{r}_2) \text{ symmetric} \end{aligned}$$

At lowest order in perturbation theory symmetric and antisymmetric functions can be easily constructed from the two degenerate states $\psi_{1s}[\mathbf{r}_1] \psi_{2s}[\mathbf{r}_2]$ and $\psi_{2s}[\mathbf{r}_1] \psi_{1s}[\mathbf{r}_2]$.

$$\Psi_{1s2s} = \frac{1}{\sqrt{2}} (\psi_{1s}[\mathbf{r}_1] \psi_{2s}[\mathbf{r}_2] \mp \psi_{2s}[\mathbf{r}_1] \psi_{1s}[\mathbf{r}_2])$$

These two wave function, that will be denoted by Ψ^A and Ψ^S are orthogonal and *do not mix* under perturbation, i.e. coulomb interaction is diagonal in this basis. We have:

$$\begin{aligned} \langle A | \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} | A \rangle &= \\ \int |\psi_{1s}[\mathbf{r}_1]|^2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} |\psi_{2s}[\mathbf{r}_2]|^2 - \int |\psi_{1s}[\mathbf{r}_1] \psi_{2s}[\mathbf{r}_1]| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} |\psi_{1s}[\mathbf{r}_2] \psi_{2s}[\mathbf{r}_2]|^2 \end{aligned}$$

$$\langle S | \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} | S \rangle = \int |\psi_{1s}[\mathbf{r}_1]|^2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} |\psi_{2s}[\mathbf{r}_2]|^2 + \int |\psi_{1s}[\mathbf{r}_1] \psi_{2s}[\mathbf{r}_1]| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} |\psi_{1s}[\mathbf{r}_2] \psi_{2s}[\mathbf{r}_2]|^2$$

For obvious reasons the first integral is named direct integral, and will be denoted by K, and the second exchange integral, and will be denoted by J. K is very similar to the integral met in ground state computation, J determines the splitting between parahelium and orthohelium. We write:

$$\langle A | \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} | A \rangle = K - J; \quad \langle S | \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} | S \rangle = K + J. \quad (14.5)$$

K, and J can be easily computed on the basis built on hydrogenic functions

$$\psi_{1s} = \frac{1}{\sqrt{4\pi}} Z^{3/2} 2 \text{Exp}[-Zr]; \quad \psi_{2s} = \frac{1}{\sqrt{4\pi}} Z^{3/2} \frac{(2 - Zr)}{2\sqrt{2}} \text{Exp}[-Zr/2]; \quad (14.6)$$

using multipole expansion, already seen in problem [13]:

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{l=0}^{\infty} \frac{1}{r_>} \left(\frac{r_<}{r_>} \right)^l P_l[\text{Cos}(\gamma)]; \quad (14.7)$$

An easy computation gives

$$K = \frac{17Z}{81}; \quad J = \frac{16Z}{729} \quad (14.8)$$

Then, at first order in perturbation theory (we report also approximate experimental data):

$$E[1s2s; S=0] = -\frac{Z^2}{2} \left(1 + \frac{1}{4} \right) + (K + J) = -\frac{5}{8} Z^2 + \frac{169}{729} Z \approx -2.036 \text{ a.u.}; \quad \text{exp} : -2.14577 \text{ a.u.}$$

$$E[1s2s; S=1] = -\frac{Z^2}{2} \left(1 + \frac{1}{4} \right) + (K - J) = -\frac{5}{8} Z^2 + \frac{137}{729} Z \approx -2.124 \text{ a.u.}; \quad \text{exp} : -2.17503 \text{ a.u.}$$

$$E[1s2s; S=0] - E[1s2s; S=1] = \frac{32Z}{729} \approx 0.088 \text{ a.u.}; \quad \text{exp} : 0.02926 \text{ a.u.}$$

We see that while ordering of levels is correct, energy differences are badly reproduced.

■ Historical remarks

It would be very difficult to overemphasize the importance of the problem of Helium atom in Quantum Mechanics.

- The disagreement between theory and experiment for highly excited Helium states marked the end of old quantum theory. In the words of Born [1], who carried the calculations with Heisenberg:

We may therefore conclude that the systematic application of the principles of the quantum theory ... gives results in agreement with experiment only in those cases where the motion of a single electron is considered; it fails even in the treatment of the motion of two electrons in the helium atom.

- In two seminal papers on helium atom [2] Heisenberg put forward the idea of the connection between spin and symmetry of the wave function, idea almost simultaneously advanced by Dirac. The observation is that if one work on unperturbed functions, and without knowing about spin statistics connection, one should treat electrostatic interaction as a perturbation on a degenerate level. In the basis

$\psi_{1s}[\mathbf{r}_1] \psi_{2s}[\mathbf{r}_2], \psi_{1s}[\mathbf{r}_2] \psi_{2s}[\mathbf{r}_1]$ the matrix will be written as

$$H_I = \begin{pmatrix} K & J \\ J & K \end{pmatrix}$$

and we know that eigenvalues are $K \pm J$, while eigenfunctions are symmetric and antisymmetric combinations. This structure agree with experimental known helium spectrum, whose spin can be detected by interaction with a magnetic field. In the second paper Heisenberg elaborate a quite sophisticated form of perturbation theory trying to explain in the new Quantum Mechanics what Old Quantum Theory was unable to explain.

- The definitive word on the argument was given by Hylleraas [3], where a variational technique were developed and a spectacular agreement with experimental data was found. We will study later variational computations.

The reader who want to go deeper in some of these aspects is referred to the book of Bethe and Salpeter [4].

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[2] W. Heisenberg: Z. Physik, 38 (1926) 411 and 39 (1926) 499.

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[4] H.A. Bethe, E.E. Salpeter: Quantum Mechanics of One-And Two-Electron Atoms, Plenum Publishing Corporation; (1977)