Homework: Due 11-24-04

This set (#10) is due on Wednesday, 11/24/2004.

■ Sakurai Chap 5: 7, 10  Merzbacher 18. 4, 5, 9  BJ 8.7

■ Merzbacher 18.4

For a constant force \( f = -\frac{\partial V}{\partial x} \), the potential is \( V = -fx + v_0 \), where \( v_0 \) is an arbitrary integration constant. The Hamiltonian is \( H = \frac{\dot{p}^2}{2m} + \frac{m\omega^2}{2} x^2 - fx + v_0 \). The problem can be solved exactly by completing the square to produce a shifted harmonic oscillator.

\[
H = \frac{\dot{p}^2}{2m} + \frac{m\omega^2}{2} x^2 - fx + v_0
\]

Choosing the integration constant \( v_0 = \frac{f^2}{2m\omega^2} \) to eliminate the constant term,

\[
H = \frac{\dot{p}^2}{2m} + \frac{m\omega^2}{2} \left( x^2 - \frac{2fx}{m\omega} x + \left( \frac{f}{m\omega} \right)^2 \right)
\]

\[
= \frac{\dot{p}^2}{2m} + \frac{m\omega^2}{2} \left( x - \frac{f}{m\omega} \right)^2
\]

\[
= \frac{\dot{p}^2}{2m} + \frac{m\omega^2}{2} x^2
\]

where \( x' = (x - \frac{f}{m\omega}) \), \( p' \) is conjugate to \( x' \). Apart from a simple change of variables this is the same as the original problem, and so the spectrum of eigenvalues is unchanged. If I hadn't used the freedom to choose \( v_0 \) there would have been a common shift to the spectrum of \( \Delta = -\frac{f^2}{2m\omega^2} \). The eigenstates are changed due to the offset in \( x \).

From the perspective of perturbation theory, one can use \( x = \frac{x_0}{\sqrt{2}} (a + a^\dagger) \), with \( x_0 = \sqrt{\frac{\hbar}{m\omega}} \) to find the first order energy shift for the \( n^{th} \) state is

\[
\Delta^1_n = \langle n | f x + v_0 | n \rangle
\]

\[
= v_0 - f \langle n | x | n \rangle
\]

\[
= v_0 - f \frac{x_0}{\sqrt{2}} \langle n | a + a^\dagger | n \rangle
\]

\[
= v_0
\]

The second order shift is

\[
\Delta^2_n = \sum_{k \neq n} \frac{|\langle n | f x + v_0 | k \rangle|^2}{E_n - E_k}
\]

\[
= f^2 \sum_{k \neq n} \frac{|\langle n | x | k \rangle|^2}{E_n - E_k}
\]

\[
= f^2 \frac{x_0^2}{2} \sum_{k \neq n} \frac{|\langle n | a + a^\dagger | k \rangle|^2}{E_n - E_k}
\]

\[
= f^2 \frac{x_0^2}{2} \sum_{n} \frac{|\langle n | a + a^\dagger | n \rangle|^2}{E_n - E_k}
\]

\[
= f^2 \frac{x_0^2}{2} \sum_{n} \frac{(n+1)}{\frac{\hbar \omega}{\hbar \omega}}
\]

\[
= -f^2 \frac{x_0^2}{2\hbar \omega} = -f^2 \frac{x_0^2}{2m\omega^2}
\]
which is the same shift as for the exact solution.

\textbf{Sakurai 5.7}

The electric dipole moment of an atom in a state $|n\rangle$ is given by $d = e \langle n | r | n \rangle$. If the atom has a dipole moment even in the absence of a field, it is said to be an intrinsic dipole moment. For an unperturbed single electron atom in the ground state, $d = 0$. In the presence of an electric field $\mathcal{E}$, however, an induced dipole moment is found proportional to the polarizability, $d = \alpha \mathcal{E}$. The dipole moment can be calculated by evaluating the expectation value for $r$ for the perturbed states.

\[
d = e \langle n | r | n' \rangle
\]

\[
= e \langle n + \delta n | r | n + \delta n \rangle
\]

\[
= e(\langle n | r | n + \delta n \rangle + \langle n + \delta n | r | n \rangle)
\]

\[
= e(\langle n | r | \delta n \rangle + \langle \delta n | r | n \rangle)
\]

\[
= e(\langle n | r | n_1 \rangle + \langle n_1 | r | n \rangle)
\]

Taking the electric field to be in the $z$-direction, so the perturbation is $V = -e\mathcal{E}z$, the first order perturbation to the eigenstate is

\[
|n_1\rangle = \sum_{k \neq n} |k\rangle \frac{\langle k | V | n \rangle}{E_n - E_k}
\]

\[
= -e\mathcal{E} \sum_{k \neq n} |k\rangle \frac{\langle k | z | n \rangle}{E_n - E_k}
\]

which gives the first order dipole moment

\[
d_z = -2 e^2 \mathcal{E} \sum_{k \neq n} \frac{|\langle k | z | n \rangle|^2}{E_n - E_k}
\]

or $\alpha = -2 e^2 \sum_{k \neq n} \frac{|\langle k | z | n \rangle|^2}{E_n - E_k}$

This can be compared to the second order energy shift

\[
\Delta_n^2 = \sum_{k \neq n} \frac{|\langle k | V | n \rangle|^2}{E_n - E_k}
\]

\[
= e^2 \mathcal{E}^2 \sum_{k \neq n} \frac{|\langle k | z | n \rangle|^2}{E_n - E_k}
\]

which, by inspection gives

\[
\Delta_n^2 = -\frac{1}{2} \mathcal{E} d_z = -\frac{1}{2} \alpha \mathcal{E}^2
\]

This is very reasonable, and in agreement with the classical energy stored in a polarizable medium under the presence of an electric field. The work done to move a charge in a field is $dE = -e\mathcal{E}dz$. Since the separation is given by

\[
d_z = -ez = \alpha \mathcal{E}, \quad dE = \mathcal{E} \alpha d\mathcal{E}
\]

or the total work done in turning the field on is

\[
E = \int e\mathcal{E} \alpha d\mathcal{E} = \frac{1}{2} \alpha \mathcal{E}^2
\]
Merzbacher 18.5

The Hamiltonian for the 3-dimensional spherically symmetric harmonic oscillator is given by

\[ H_0 = \frac{p^2}{2m} + \frac{\hbar \omega}{2} x^2 = \left( \frac{p_x^2}{2m} + \frac{\hbar \omega}{2} x^2 \right) + \left( \frac{p_y^2}{2m} + \frac{\hbar \omega}{2} y^2 \right) + \left( \frac{p_z^2}{2m} + \frac{\hbar \omega}{2} z^2 \right) \]

where the three frequencies are degenerate in the symmetric case. Raising and lowering operators can be defined, e.g. \( a_\pm = (x + i p_x) \) etc, so that

\[ H_0 = \hbar \omega_x (N_x + \frac{1}{2}) + \hbar \omega_y (N_y + \frac{1}{2}) + \hbar \omega_z (N_z + \frac{1}{2}) \]

where the last line is for the symmetric case. The eigenstates of \( H_0 \) can be labeled by \( |n_x, n_y, n_z\rangle \), the eigenvalues of three number operators \( N_x, N_y, N_z \). The ground state is \( |000\rangle \) with energy \( E_0 = \frac{3}{2} \hbar \omega \), the first three excited states are \( |100\rangle, |010\rangle, |001\rangle \) with energy \( E_1 = \frac{5}{2} \hbar \omega \).

For the problem at hand it is specified that the oscillator has a small asymmetry which may be realized as \( \omega_z = (1 + \delta) \omega \), and that a magnetic field in the \( x \)-direction leads to a Zeeman splitting of the levels. The energy eigenvalues of the \( N = 1 \) states are to be found using perturbation theory.

Treated by itself, either perturbation could be dealt with exactly

a) For the case of slight anisotropy, the exact solutions are still obtained for the \( |n_x, n_y, n_z\rangle \) basis with energies

\[ H = \hbar \omega_x (N_x + \frac{1}{2}) + \hbar \omega_y (N_y + \frac{1}{2}) + \hbar \omega_z (N_z + \frac{1}{2}) \]

\[ = \hbar \omega (N + \frac{3}{2}) + \delta \hbar \omega (N_z + \frac{1}{2}) \]

b) For the case of a magnetic field, let the field be in the \( z \)-direction. First, however, instead of using a basis \( |n_x, n_y, n_z\rangle \) it must also be possible to find unperturbed states denoted by \( |nlm\rangle \) which reflect the underlying spherical symmetry. Indeed, defining the operators \( a_\pm = \mp (a_x \pm ia_y) \), \( a_0 = a_3 \), one may reexpress the number operator as \( N = N_x + N_0 + N_- \). The operators \( a_+, a_0, a_- \) form the three components of a rank-1 tensor operator. Accordingly, by the Wigner-Eckart theorem when they operate on the ground state, which has \( l = m = 0 \), the first excited states must constitute the three states of an \( l = 1 \) representation. Further, higher excited states can also be decomposed into representations of angular momentum, e.g. the 6 states with \( N = 2 \) will form \( l = 0 \) and \( l = 2 \) representations. The azimuthal quantum numbers must satisfy an \( m \) summation formula, \( m = N_x - N_- \). Accordingly, one can write the Hamiltonian with \( B_z \) in the spherical basis as

\[ H = \hbar \omega (N_x + N_- + N_0 + \frac{3}{2}) + \frac{eB}{2mc} L_z \]

\[ = \hbar \omega (N_x + N_- + N_0 + \frac{3}{2}) + \frac{eB}{2mc} (N_+ - N_-) \]

\[ = \hbar \omega (N + \frac{3}{2}) + \frac{eB}{2mc} (N_+ - N_-) \]

c) Return now to the problem with both \( B \) and the anisotropy. For convenience of notation keep \( B_z \) and shift the anisotropy to \( \omega_x \), instead of the other way around. Working with the \( |jm\rangle \) basis states

\[ H = \hbar \omega (N + \frac{3}{2}) + \delta \hbar \omega (N_x + \frac{1}{2}) + \frac{eB}{2mc} (N_+ - N_-) \]
In this basis, the perturbation due to \( B_z \) is diagonal, but that due to \( N_z \) is not. \( N_z \) can be expressed as

\[
N_z = a_+ a_-
= \left( a_+^\dagger - a_+^\dagger \right) (a_+ - a_-)
= \frac{1}{2} (N_+ + N_-) - \frac{1}{2} \left( a_+^\dagger a_- + a_-^\dagger a_+ \right)
\]

so the matrix representation of the Hamiltonian for the \( N = 1 \) subspace, with rows and columns ordered +, 0, \(-1\) is

\[
H_0 = \hbar \omega \begin{pmatrix}
\frac{5}{2} & 0 & 0 \\
0 & \frac{5}{2} & 0 \\
0 & 0 & \frac{5}{2}
\end{pmatrix},
H_x = \delta \hbar \omega \begin{pmatrix}
1 & 0 & -\frac{1}{2} \\
0 & \frac{1}{2} & 0 \\
-\frac{1}{2} & 0 & 1
\end{pmatrix},
H_B = \frac{eB}{2mc} \begin{pmatrix}
1 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & -1
\end{pmatrix}
\]

This can be solved exactly by diagonalizing, and this is appropriate for the general degenerate analysis when the two perturbations are comparable. Using \( \Delta = \left( \delta \hbar \omega \right)^2 + \left( \frac{eB}{2mc} \right)^2 \), the energies are

\[
E_+ = \frac{5}{2} \hbar \omega + \delta \hbar \omega \pm \Delta
E_0 = \frac{5}{2} \hbar \omega + \frac{1}{2} \delta \hbar \omega
\]

Alternatively, in this basis there is no degeneracy once the \( B \) term is turned on. Accordingly, one can use first order perturbation theory if \( \delta < B \)

\[
E_+ = \frac{5}{2} \hbar \omega + \delta \hbar \omega + \frac{eB}{2mc}
E_0 = \frac{5}{2} \hbar \omega + \frac{1}{2} \delta \hbar \omega
E_- = \frac{5}{2} \hbar \omega + \delta \hbar \omega - \frac{eB}{2mc}
\]

Or, if \( B < \delta \), it would make more sense to work in the cartesian basis. Now the rows and columns are for \( x, y, z \)

\[
H_0 = \hbar \omega \begin{pmatrix}
\frac{5}{2} & 0 & 0 \\
0 & \frac{5}{2} & 0 \\
0 & 0 & \frac{5}{2}
\end{pmatrix},
H_x = \delta \hbar \omega \begin{pmatrix}
\frac{3}{2} & 0 & 0 \\
0 & \frac{1}{2} & 0 \\
0 & 0 & \frac{1}{2}
\end{pmatrix},
H_B = \frac{eB}{2mc} \begin{pmatrix}
0 & -i & 0 \\
i & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}
\]

Note: in principle there is a \( B^2 \) term which comes from the \( A \cdot A \) term of the Hamiltonian. This term is small compared to the other \( B \) terms, unless \( \delta > \omega \), in which case the problem is no longer perturbative.

- **Merzbacher 18.9**

The relativistic energy is \( E^2 = p^2 + m^2 \). Expanding this around \( m \) as an operator equation

\[
E = m + \frac{p^2}{2m} - \frac{(p^2)^2}{8m^3} \ldots
\]

Treating the \( p^4 \) term as a perturbation, the leading order energy shift for the hydrogen 1 \( s \) state is

\[
\Delta = -\frac{1}{8m^3} \langle 1 \ s | p^2 | 1 \ s \rangle
\]

Setting \( \hbar = c = 1 \) for the moment, one can use the relation that \( H_0 = \frac{p^2}{2m} - \frac{\alpha}{r} \), with \( \alpha = \frac{1}{137} \). Rearranging, one has

\[
p^2 = 2m(H_0 + \frac{\alpha}{r})
\]

so that
\[ \Delta = -\frac{1}{2m} \langle 1 \mid s \mid (H_0 + \frac{\alpha}{r} + \frac{\alpha^3}{r^2}) + 1 \rangle \]
\[ = -\frac{1}{2m} \langle 1 \mid s \mid (E_0^2 + 2 E_0 \frac{\alpha}{r} + \frac{\alpha^2}{r^2}) + 1 \rangle \]
where \( E_0 = -\frac{\alpha^2}{2m} \). The matrix elements for \( \frac{1}{r} \) and \( \frac{1}{\alpha^2} \) are
\[ \langle 1 \mid \frac{1}{r} \mid 1 \rangle = \int r^2 d r \frac{1}{r} \frac{4}{a_0^3} e^{-2r/a_0} \]
\[ = \frac{1}{2} \left( \frac{2}{a_0} \right)^n \int u^{2-n} e^{-u} du \]
where the Bohr radius is given by \( a_0 = \frac{1}{\alpha m} \).
\[ \langle 1 \mid \frac{1}{\alpha^2} \mid 1 \rangle = \frac{1}{2} \left( \frac{2}{a_0} \right)^2 \int u^0 e^{-u} du = \frac{2}{a_0^2} = 2 \alpha^2 m^2 \]
Combining with the above results
\[ \Delta = -\frac{1}{2m} \langle 1 \mid s \mid (E_0^2 + 2 E_0 \frac{\alpha}{r} + \frac{\alpha^2}{r^2}) + 1 \rangle \]
\[ = -\frac{1}{2m} \left( \frac{4}{a}^2 \right) m^2 - 2 \frac{\alpha^2}{2} m \cdot \alpha \cdot \alpha m + \alpha^2 \cdot 2 \alpha^2 m^2 \]
\[ = -\frac{1}{2m} \alpha \cdot \alpha m^2 (\frac{1}{4} - 1 + 2) \]
\[ = -\frac{5}{8} \alpha \cdot \alpha m = -5 \frac{E_0^2}{2m} \]

■ Sakurai 5.10

The Hamiltonian is \( H = H_0 + V_1 \), where \( H_0 = \frac{p^2}{2m} + \frac{\alpha^2}{2m} + V_0 \) and \( V_0(x, y) = 0 \) for \( 0 < x, y < a \) and \( \infty \) outside that region. The unperturbed states are denoted by \( |n_x n_y \rangle \) with \( n_x, n_y \) allowed to be positive integers. The wavefunctions are
\[ \langle xy \mid n_x n_y \rangle = \frac{2}{a} \sin(k_n x) \sin(k_n y) \]
where \( k_n = \frac{\pi}{a} n \). The energies are \( E_{n_x n_y} = \frac{\hbar^2 n_x^2 + n_y^2}{2ma^2} = E_0(n_x^2 + n_y^2) \).

The perturbation is \( V_1 = \lambda xy \).

a) The three lowest energy states are \( |11 \rangle, |21 \rangle, |12 \rangle \), with energies \( E_{11} = 2 E_0, E_{12} = E_{21} = 5 E_0 \). The states \( |21 \rangle, |12 \rangle \) are degenerate.

b-i) The \( |11 \rangle \) is not degenerate, so it is first order if expectation of perturbation \( V_1 \) is non-vanishing, i.e. if \( \Delta_{11} = \langle 11 \mid \lambda xy \mid 11 \rangle \neq 0 \). The other two states are degenerate, so the question of 1st or 2nd order depends on diagonalizing \( V_1 \) in the degenerate subspace.

b-ii) For the \( |11 \rangle \) the first order energy shift is given by
\[ \Delta_{11} = \langle 11 \mid \lambda xy \mid 11 \rangle = \lambda \frac{4}{\alpha^2} \int_0^a dx \sin^2(k_1 x) \int_0^a dy \sin^2(k_1 y) y \]
The integrals are given by \( \int_0^a dx \sin^2(k_1 x) = \int_0^a dx \sin^2(k_1 x) (x - \frac{a}{2}) + \frac{a}{2} \int_0^a dx \sin^2(k_1 x) = 0 + \frac{a}{2} \frac{\pi}{2} = \frac{\pi a}{4} \), so
\[ \Delta_{11} = \lambda \frac{\pi a}{4} \]
For the degenerate |12⟩, |21⟩ states one must begin by finding linear combinations which diagonalize \( V_1 \). In the unperturbed basis \( V_1 \) is given by

\[
V_1 = \lambda \begin{pmatrix} I_{11}^x & I_{12}^x & I_{21}^x & I_{22}^x \\ I_{11}^y & I_{12}^y & I_{21}^y & I_{22}^y \\ I_{11}^z & I_{12}^z & I_{21}^z & I_{22}^z \end{pmatrix}
\]

where the integrals are given by

\[
I_{11} = \frac{2}{a} \int_0^a dx \sin^2(k_1 x) x = \frac{a}{2} \\
I_{22} = \frac{2}{a} \int_0^a dx \sin^2(k_2 x) x = \frac{a}{2} \\
I_{12} = I_{21} = \frac{2}{a} \int_0^a dx \sin(k_1 x) \sin(k_2 x) x = -\frac{16}{9\pi^2} a
\]

with these integrals, and \( b = \left( \frac{32}{9\pi^2} \right)^2 \),

\[
V_1 = \lambda \frac{a^2}{4} \begin{pmatrix} 1 & b \\ b & 1 \end{pmatrix}
\]

The new eigenstates are

\[
|\pm\rangle = \frac{1}{\sqrt{2}} \left( |12\rangle \pm |21\rangle \right)
\]

and the energy shifts are

\[
\Delta_{\pm} = \lambda \frac{a^2}{4} \left( 1 \pm b \right)
\]

The degenerate states have an energy shift, and the degeneracy is split by about 10%.

b-iii) In the figure, the energy axis is scaled to \( E_0 = \frac{b^2 \pi^2}{2ma^2} \), and the strength of the perturbation is scaled to \( \Delta_0 = \frac{a^2}{4} \). The black line is \( E_{11} \). The red/blue lines are \( E_{\pm} \). The result is only valid to first order in \( \lambda \).


**BJ 8.7**

The potential energy of an electron in the presence of the nuclear charge distribution is

\[
V = -\int_{\infty}^r F(r') dr'
\]
where the force is given by

\[ F(r) = -\frac{\alpha Q(r)}{r^2} = -\frac{\alpha}{\gamma} \int_0^r 4\pi r^2 \rho(r) \, dr \]

If the total charge is \( Q \), and \( \rho \) is constant within the radius \( R \), then \( Q(r) = \frac{Q}{R^2} \, Q \), and for \( r < R \)

\[ V(r) = -\alpha \left( \frac{Q}{R^2} \int_0^r 4\pi r^2 \, dr + \int_r^\infty \frac{Q(r)}{r^2} \, dr \right) \\
= -\alpha Q \left( \frac{1}{R} - \frac{1}{2} \frac{r^2}{R^2} - \frac{r^2}{R^2} \right) \\
= -\alpha Q \frac{1}{2R} \left( 3 - \frac{r^2}{R^2} \right) \]

This potential deviates from the pure \( \frac{1}{r} \) coulomb potential, by \( V_1 = V - \left( -\frac{\alpha Q}{r} \right) \).

\[ V_1 = \begin{cases} 
\alpha Q \left( \frac{1}{r} - \frac{3}{2R} + \frac{r^2}{2R^2} \right) & r < R \\
0 & r > R \end{cases} \]

Even though this term is not small (in fact it is infinite as \( r \to 0 \)), it may still be treated perturbatively since the affected volume is so small. The energy perturbation is then

\[ \Delta = \langle nlm | V_1 | nlm \rangle = \int r^2 \, dR R_{nlm}^2(r) \, V_1(r) = \alpha Q \int_0^R dR R_{nlm}^2(r) \, r^2 \left( \frac{1}{r} - \frac{3}{2R} + \frac{r^2}{2R^2} \right) \]

Now, since the nuclear size is so much smaller than the atomic size, \( R \ll a_0 \), it is reasonable to approximate \( R_{nl}(r) \approx R_{nl}(0) \)

\[ \Delta = \alpha Q R_{nl}^2(0) \int_0^R dR R^2 \left( \frac{1}{r} - \frac{3}{2R} + \frac{r^2}{2R^2} \right) = \alpha Q R_{nl}^2(0) R^2 \left( \frac{1}{2} - \frac{3}{4} + \frac{1}{4} \right) \]

\[ = \frac{\alpha}{10} Q R_{nl}^2(0) R^2 \]

At the origin \( R_{nl} \) vanishes for \( l \neq 0 \) due to the effective centrifugal \( \frac{\hbar(l+\frac{1}{2})}{r^2} \) potential. Next, let us consider the correction for the ground state where \( R_{10}^2 = 4 \frac{a_0^9}{6} \). Since the problem deals with a nucleus of charge \( Q \), the wavefunction should include the scaling of the Bohr radius with \( Q \), \( a_Q = \frac{a_0}{Q} \), so that at \( r = 0 \), \( R_{10}^2 = 4 \frac{Q}{a_0^9} \), or

\[ \Delta_{10} = \frac{2}{3} \alpha Q^4 \frac{R^2}{a_0^9} \]

To be honest, I don't know how the \( l = 0 \) wave functions scale with increasing principle quantum number \( n \). From the solution supplied I infer

\[ R_{n0}(r = 0) = \frac{1}{n^{1/2}} R_{10}(r = 0) \]

so that \( \Delta_{nl} = \frac{2}{5} \alpha Q^4 \frac{R^2}{n^{1/2} a_0^9} \delta_{00} \)

I suspect that this applies only to a single electron atom, since a full discussion of screening by inner shell electrons is beyond the scope of this problem.
- stuff