

Physics 221A
Fall 2010
Notes 21
Bound-State Perturbation Theory

1. Introduction

Bound state perturbation theory applies to the bound states of perturbed systems, for which the energy levels are discrete and separated from one another. The system may also have a continuous spectrum, but the interest is attached to the discrete states. The effects of perturbations on states of the continuous spectrum, or on discrete states imbedded in the continuum, require different techniques, such as time-dependent perturbation theory.

The version of bound-state perturbation theory that you are probably familiar with is called Rayleigh-Schrödinger perturbation theory. In these notes, we will begin with a variation on Rayleigh-Schrödinger perturbation theory, called Brillouin-Wigner perturbation theory. The Brillouin-Wigner theory is simpler and less messy to derive than the Rayleigh-Schrödinger theory, and it also gives more accurate answers in many circumstances. Its disadvantage is that the unknown energy levels are given only implicitly, in terms of the solutions of nonlinear equations. But if explicit formulas for the energy levels are desired, it is easy to expand the solutions in powers of the perturbation parameter, whereupon the results of the Rayleigh-Schrödinger theory are recovered. In my opinion, this is the easiest and most elegant way to derive Rayleigh-Schrödinger perturbation theory.

2. The Unperturbed and Perturbed States

We consider an unperturbed Hamiltonian H_0 with eigenvalues ϵ_k and eigenstates $|k\alpha\rangle$, where α is an index introduced to resolve degeneracies, so that

$$H_0|k\alpha\rangle = \epsilon_k|k\alpha\rangle. \tag{1}$$

See Fig. 1, in which the unperturbed levels ϵ_k are illustrated on a vertical axis. We pick one of these levels ϵ_n for study, so the index n will be fixed for the following discussion. We denote the eigenspace of the unperturbed system corresponding to eigenvalue ϵ_n by \mathcal{H}_n , so that the unperturbed eigenkets $\{|n\alpha\rangle, \alpha = 1, 2, \dots\}$ form a basis in this space.

We take the perturbed Hamiltonian to be $H = H_0 + \lambda H_1$, where λ is a formal expansion parameter that we allow to vary between 0 and 1 to interpolate between the unperturbed and perturbed system. When the perturbation is turned on, the unperturbed energy level ϵ_n may split and shift. We denote one of the exact energy levels that grows out of ϵ_n by E , as shown in Fig. 1. We let $|\psi\rangle$ be an exact energy eigenket corresponding to energy E , so that

$$H|\psi\rangle = (H_0 + \lambda H_1)|\psi\rangle = E|\psi\rangle. \tag{2}$$

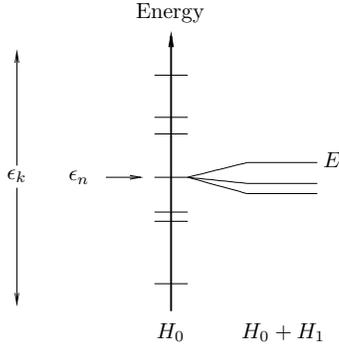


Fig. 1. The energy levels ϵ_k of the unperturbed system H_0 are shown on a vertical axis. These levels are degenerate in general. One of these, ϵ_n , is selected out for study. When the perturbation H_1 is turned on, level ϵ_n may split and shift. The energy level E of the perturbed system $H_0 + \lambda H_1$ is one that grows out of ϵ_n as the perturbation is turned on.

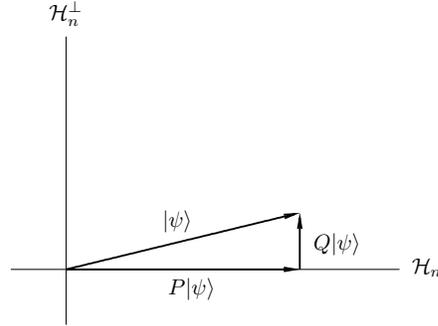


Fig. 2. Subspace \mathcal{H}_n is the unperturbed eigenspace for level ϵ_n , and \mathcal{H}_n^\perp is the orthogonal subspace. Projectors P and Q project onto \mathcal{H}_n and \mathcal{H}_n^\perp , respectively. The exact eigenstate lies approximately in \mathcal{H}_n , with a small correction $Q|\psi\rangle$ orthogonal to this subspace.

Both E and ψ are understood to be functions of λ ; as $\lambda \rightarrow 0$, E approaches ϵ_n and $|\psi\rangle$ approaches some state lying in \mathcal{H}_n .

It helps to have a picture of the perturbation problem in terms of the geometry of Hilbert space. We break the Hilbert space into the subspace \mathcal{H}_n and its orthogonal complement which we denote by \mathcal{H}_n^\perp . The latter space is spanned by the unperturbed eigenkets $\{|k\alpha\rangle\}$ for all $k \neq n$. Since the perturbation is small, the exact eigenket $|\psi\rangle$ presumably lies nearly in \mathcal{H}_n , with only a small component orthogonal to \mathcal{H}_n , as illustrated in Fig. 2. The components of $|\psi\rangle$ parallel and perpendicular to \mathcal{H}_n are conveniently expressed in terms of the projector P onto the subspace \mathcal{H}_n and the orthogonal projector Q , defined by

$$P = \sum_{\alpha} |n\alpha\rangle\langle n\alpha|, \quad (3)$$

and

$$Q = \sum_{\substack{k \neq n \\ \alpha}} |k\alpha\rangle\langle k\alpha|. \quad (4)$$

These projectors satisfy $P^2 = P$, $Q^2 = Q$, $PQ = QP = 0$ and $P + Q = 1$. They also commute with H_0 ,

$$[P, H_0] = [Q, H_0] = 0, \quad (5)$$

since they project onto eigenspaces of H_0 . In terms of these projectors, the components of $|\psi\rangle$ parallel and perpendicular to \mathcal{H}_n are $P|\psi\rangle$ and $Q|\psi\rangle$, respectively, as illustrated in Fig. 2.

The component $P|\psi\rangle$ of the exact eigenstate $|\psi\rangle$ lies in the unperturbed eigenspace, and thus is itself an unperturbed eigenstate. It is therefore a linear combination of the known unperturbed eigenstates $\{|n\alpha\rangle, \alpha = 1, 2, \dots\}$, and is easily characterized. The orthogonal component $Q|\psi\rangle$, on

the other hand, is harder to find. In the following we will think of $P|\psi\rangle$ as the easy part of $|\psi\rangle$ and $Q|\psi\rangle$ as the hard part, and attempt to solve for the hard part $Q|\psi\rangle$ (or else the total solution $|\psi\rangle = P|\psi\rangle + Q|\psi\rangle$) in terms of the easy part $P|\psi\rangle$. It turns out it is possible to write a neat power series expansion for this solution, Eq. (16) below.

As a first step in the derivation of this series, we rearrange Eq. (2) in the form,

$$(E - H_0)|\psi\rangle = \lambda H_1|\psi\rangle. \quad (6)$$

We would like to divide this equation by $E - H_0$ to solve for $|\psi\rangle$, but before proceeding we must examine $(E - H_0)^{-1}$ to see if it is well behaved.

3. The Inverse of $E - H_0$ on \mathcal{H}_n^\perp

The operator $(E - H_0)^{-1}$ is a function of the operator H_0 , which according to Eq. (1.129) can be written in terms of the eigenvalues and projectors of H_0 ,

$$\frac{1}{E - H_0} = \sum_{k\alpha} \frac{|k\alpha\rangle\langle k\alpha|}{E - \epsilon_k}. \quad (7)$$

The resulting expression, however, is meaningless if the exact eigenvalue E should equal any of the unperturbed eigenvalues ϵ_k . In that case, one or more denominators vanish, indicating that $E - H_0$ does not possess an inverse. Even if none of the denominators vanishes, nevertheless the exact eigenvalue E is presumably close to the unperturbed eigenvalue ϵ_n , and therefore the terms $k = n$ in Eq. (7) are large (and these terms diverge at $\lambda = 0$, where $E = \epsilon_n$).

In order to avoid small or vanishing denominators, and to work with operators that are guaranteed to be well defined, we define a new operator R which is Eq. (7) with the terms $k = n$ suppressed:

$$R = \sum_{\substack{k \neq n \\ \alpha}} \frac{|k\alpha\rangle\langle k\alpha|}{E - \epsilon_k}. \quad (8)$$

The operator R is closely related to the Green's operators that we shall consider later in the course, when we take up scattering theory.

It is possible that $E - \epsilon_n$ is not the only small or vanishing denominator in Eq. (7). For example, if there are other unperturbed energy levels ϵ_k lying close to ϵ_n , then the perturbation could push the exact energy E near to or past some of these other levels, and then other small denominators would result in Eq. (7). This will certainly happen if the perturbation is large enough. For the time being we will assume this does not happen, so that Eq. (8) is free of small denominators. This is the situation illustrated in Fig. 1. When this is not the case we shall refer to “nearly degenerate perturbation theory,” which is discussed in Sec. 7.

The operator R satisfies

$$\begin{aligned} PR &= RP = 0, \\ QR &= RQ = R, \end{aligned} \quad (9)$$

and

$$R(E - H_0) = (E - H_0)R = Q. \quad (10)$$

These equations show that R vanishes on the subspace \mathcal{H}_n , while it is the inverse of $E - H_0$ on the subspace \mathcal{H}_n^\perp . Note that Q is just the identity operator on \mathcal{H}_n^\perp .

4. A series for $|\psi\rangle$ in terms of $P|\psi\rangle$

We return now to Eq. (6) and multiply through by R , using Eq. (10). This gives

$$Q|\psi\rangle = \lambda RH_1|\psi\rangle, \quad (11)$$

which expresses the “hard” part of the exact eigenstate $Q|\psi\rangle$ in terms of the total exact eigenstate $|\psi\rangle$. To turn this into something more useful, we first add $P|\psi\rangle$ to both sides, obtaining

$$|\psi\rangle = P|\psi\rangle + \lambda RH_1|\psi\rangle. \quad (12)$$

This expresses the exact eigenket $|\psi\rangle$ in terms of its projections onto \mathcal{H}_n and \mathcal{H}_n^\perp , of which the second term is a small correction. It is not an explicit solution for $|\psi\rangle$ since $|\psi\rangle$ occurs on the right hand side, but it can be converted into a power series solution by a method of successive approximation.

In particular, note that if we neglect the second term in Eq. (12), which is of order λ , we obtain $|\psi\rangle = P|\psi\rangle$, which is correct to lowest order. To improve on the approximation, we substitute the left hand side of Eq. (12) into the second term on the right hand side, obtaining,

$$|\psi\rangle = P|\psi\rangle + \lambda RH_1P|\psi\rangle + \lambda^2 RH_1RH_1|\psi\rangle, \quad (13)$$

which is still an exact equation. Now all terms on the right hand side except the last one involve the “easy” part $P|\psi\rangle$ of the exact eigenstate, and only the final term, which is second order in the perturbation, involves $|\psi\rangle$. If we neglect that term, we obtain an expression for $|\psi\rangle$ in terms of $P|\psi\rangle$ that is valid to first order in λ . Continuing this way, we can substitute the left hand side of Eq. (12) into the last term in Eq. (13), to push the hard term to fourth order in λ , etc. The result is a formal power series for the solution $|\psi\rangle$ in terms of the easy part $P|\psi\rangle$.

Another way to get the same thing is to rearrange Eq. (12),

$$(1 - \lambda RH_1)|\psi\rangle = P|\psi\rangle, \quad (14)$$

so that

$$|\psi\rangle = \left(\frac{1}{1 - \lambda RH_1} \right) P|\psi\rangle. \quad (15)$$

The inverse operator is then easily expanded in a series,

$$\begin{aligned} |\psi\rangle &= \sum_{r=0}^{\infty} \lambda^r (RH_1)^r P|\psi\rangle \\ &= P|\psi\rangle + \lambda RH_1P|\psi\rangle + \lambda^2 RH_1RH_1P|\psi\rangle + \dots \end{aligned} \quad (16)$$

This is the basic series out of which all the results of perturbation theory are constructed. The series might not converge, but in perturbation theory we do not necessarily need convergent series.

5. Nondegenerate Perturbation Theory

In nondegenerate perturbation theory the level ϵ_n of H_0 is nondegenerate. Then the index α is not needed for the level ϵ_n , and we can write simply $|n\rangle$ for the corresponding eigenstate. We retain α for the other levels $k \neq n$, since these may still be degenerate. Then since the space \mathcal{H}_n is 1-dimensional and is spanned by $|n\rangle$, we must have $P|\psi\rangle = c|n\rangle$, where c is some constant. It is obvious from Fig. 2 that $|\psi\rangle$ and $P|\psi\rangle$ cannot both be normalized, since one is the base and the other the hypotenuse of a right triangle. In the following it is convenient to take $c = 1$ so that

$$P|\psi\rangle = |n\rangle, \quad (17)$$

where we assume that $|n\rangle$ and the other unperturbed eigenstates are normalized. This is the most convenient normalization convention for nondegenerate perturbation theory, but it means that $|\psi\rangle$ is not normalized, in fact from Fig. 2 it is clear that $\langle\psi|\psi\rangle > 1$. After we are done with the perturbation expansion, we are free to normalize $|\psi\rangle$ in the usual way. With this normalization convention, we have

$$\langle n|\psi\rangle = 1, \quad (18)$$

which is also obvious from Fig. 2.

Now the series (16) becomes

$$\begin{aligned} |\psi\rangle &= \sum_{r=0}^{\infty} \lambda^r (RH_1)^r |n\rangle \\ &= |n\rangle + \lambda RH_1 |n\rangle + \lambda^2 RH_1 RH_1 |n\rangle + \dots \\ &= |n\rangle + \lambda \sum_{\substack{k \neq n \\ \alpha}} |k\alpha\rangle \frac{\langle k\alpha|H_1|n\rangle}{E - \epsilon_k} \\ &\quad + \lambda^2 \sum_{\substack{k \neq n \\ \alpha}} \sum_{\substack{k' \neq n \\ \alpha'}} |k\alpha\rangle \frac{\langle k\alpha|H_1|k'\alpha'\rangle \langle k'\alpha'|H_1|n\rangle}{(E - \epsilon_k)(E - \epsilon_{k'})} + \dots \end{aligned} \quad (19)$$

which expresses the exact eigenket $|\psi\rangle$ as an infinite series in terms of the unperturbed eigenket $|n\rangle$. However, the operator R still involves the unknown energy level E , which appears in the denominators, so Eq. (19) is still not an explicit solution for the exact eigenket $|\psi\rangle$.

To find an equation for E , we multiply Eq. (2) on the left by $\langle n|$ and use Eq. (18) to get

$$\langle n|(E - H_0)|\psi\rangle = E - \epsilon_n = \lambda \langle n|H_1|\psi\rangle, \quad (20)$$

and then we substitute Eq. (19) into this. Thus we find

$$\begin{aligned} E &= \epsilon_n + \lambda \langle n|H_1|n\rangle + \lambda^2 \langle n|H_1 RH_1|n\rangle + \lambda^3 \langle n|H_1 RH_1 RH_1|n\rangle + \dots \\ &= \epsilon_n + \lambda \langle n|H_1|n\rangle + \lambda^2 \sum_{\substack{k \neq n \\ \alpha}} \frac{\langle n|H_1|k\alpha\rangle \langle k\alpha|H_1|n\rangle}{E - \epsilon_k} \end{aligned}$$

$$+ \lambda^3 \sum_{\substack{k \neq n \\ \alpha}} \sum_{\substack{k' \neq n \\ \alpha'}} \frac{\langle n | H_1 | k \alpha \rangle \langle k \alpha | H_1 | k' \alpha' \rangle \langle k' \alpha' | H_1 | n \rangle}{(E - \epsilon_k)(E - \epsilon_{k'})} + \dots \quad (21)$$

Since the unknown exact energy E still appears in the denominators on the right hand side of this equation, this is not an explicit solution for E . But Eq. (21) does give E explicitly through $O(\lambda)$,

$$E = \epsilon_n + \lambda \langle n | H_1 | n \rangle + O(\lambda^2), \quad (22)$$

which agrees with the usual result of Rayleigh-Schrödinger perturbation theory. If we want the energy correct through $O(\lambda^2)$, we can substitute the zeroth order approximation for E , namely, $E = \epsilon_n$, into the denominator of the $O(\lambda^2)$ term in Eq. (21), whereupon we find

$$E = \epsilon_n + \lambda \langle n | H_1 | n \rangle + \lambda^2 \sum_{\substack{k \neq n \\ \alpha}} \frac{\langle n | H_1 | k \alpha \rangle \langle k \alpha | H_1 | n \rangle}{\epsilon_n - \epsilon_k} + O(\lambda^3), \quad (23)$$

which agrees with Rayleigh-Schrödinger theory through $O(\lambda^2)$. Similarly, if we wish the energy correct to $O(\lambda^3)$, we can substitute the first order expression (22) for E into the denominator of the $O(\lambda^2)$ term in Eq. (21), and the zeroth order expression $E = \epsilon_n$ into the $O(\lambda^3)$ term, etc. When the denominators are expanded out in powers of λ , the results of Rayleigh-Schrödinger perturbation theory are recovered. At third order and beyond, the expressions of the Rayleigh-Schrödinger theory are more complicated than those of the Brillouin-Wigner theory, because of the extra terms that come from expanding the denominators.

Once the energy E has been determined in this manner, we can go back to Eq. (19) and obtain the eigenkets. For example, through first order we have

$$|\psi\rangle = |n\rangle + \lambda \sum_{\substack{k \neq n \\ \alpha}} |k\alpha\rangle \frac{\langle k\alpha | H_1 | n \rangle}{\epsilon_n - \epsilon_k} + O(\lambda^2), \quad (24)$$

which again is the usual result from Rayleigh-Schrödinger perturbation theory.

6. Degenerate Perturbation Theory

In the case that the unperturbed energy level ϵ_n is degenerate, the projection of the exact eigenket $|\psi\rangle$ onto \mathcal{H}_n must be a linear combination of the unperturbed eigenkets $|n\alpha\rangle$,

$$P|\psi\rangle = \sum_{\alpha} |n\alpha\rangle c_{\alpha}, \quad (25)$$

where c_{α} are the expansion coefficients. Since $Q|\psi\rangle$ is orthogonal to all the kets $|n\alpha\rangle$, we have

$$\langle n\alpha | P|\psi\rangle = \langle n\alpha | \psi\rangle = c_{\alpha}. \quad (26)$$

To obtain an equation for the c_{α} 's, we multiply Eq. (2) on the left by $\langle n\alpha |$ and use Eq. (26) to obtain,

$$\langle n\alpha | (E - H_0) |\psi\rangle = (E - \epsilon_n) c_{\alpha} = \lambda \langle n\alpha | H_1 | \psi\rangle. \quad (27)$$

We substitute Eq. (16) into this, using Eq. (25) for $P|\psi\rangle$, and we find

$$\begin{aligned}
(E - \epsilon_n)c_\alpha &= \lambda \sum_{\beta} \langle n\alpha|H_1|n\beta\rangle c_\beta + \lambda^2 \sum_{\beta} \langle n\alpha|H_1RH_1|n\beta\rangle c_\beta + \dots \\
&= \lambda \sum_{\beta} \langle n\alpha|H_1|n\beta\rangle c_\beta \\
&\quad + \lambda^2 \sum_{\beta} \sum_{\substack{k \neq n \\ \gamma}} \frac{\langle n\alpha|H_1|k\gamma\rangle \langle k\gamma|H_1|n\beta\rangle}{E - \epsilon_k} c_\beta + \dots
\end{aligned} \tag{28}$$

This equation must be solved simultaneously for the eigenvalues E and the unknown expansion coefficients c_α .

If we truncate the series (28) at first order, we see that the corrections $E - \epsilon_n$ to the energies are determined as the eigenvalues of the $g \times g$ matrix $\langle n\alpha|H_1|n\beta\rangle$, $\alpha, \beta = 1, \dots, g$, where g is the degeneracy of the unperturbed level ϵ_n , and the coefficients c_α are the corresponding eigenvectors. This determines the energies to first order, but the coefficients c_α only to zeroth order. Then by using Eq. (25), $P|\psi\rangle$ becomes known to zeroth order, and this can be substituted into Eq. (16) to determine $Q|\psi\rangle$ to first order.

The first order matrix $\langle n\alpha|H_1|n\beta\rangle$ may or may not have degeneracies itself. If it does not, then all degeneracies are lifted at first order; if it does, the remaining degeneracies may be lifted at a higher order, or may persist to all orders. Degeneracies that persist to all orders are almost always due to some symmetry of the system, which can usually be recognized at the outset.

To proceed to second order, we may substitute the zeroth order solution $E = \epsilon_n$ into the denominators of the second order term in Eq. (28) and truncate the series at this order. We then obtain a new eigenvalue-eigenvector problem for the unknown energy corrections $E - \epsilon_n$ and coefficients c_α , which differs from the one we had at first order by the addition of a second order matrix as a correction to the matrix $\langle n\alpha|H_1|n\beta\rangle$ that we had at first order. We can evaluate the eigenvalues and eigenvectors of the sum of these two matrices by standard matrix techniques, or we can regard the new eigenvalue-eigenvector problem as a new problem in bound state perturbation theory, in which the first order matrix $\langle n\alpha|H_1|n\beta\rangle$ plays the role of a new unperturbed Hamiltonian, say, \tilde{H}_0 , and the second order matrix plays the role of a new perturbation, say, \tilde{H}_1 . We will have to use either the nondegenerate or degenerate versions of this theory, depending on whether or not all degeneracies of the original Hamiltonian H_0 were lifted at first order. In any case, once the energies E and coefficients c_α have been determined to some order, they can be substituted into Eq. (25) and (16) to determine both $P|\psi\rangle$ and $Q|\psi\rangle$.

7. Nearly Degenerate Perturbation Theory

Now let us consider the case in which the unperturbed levels of H_0 , while not technically degenerate, are close to one another. This often happens in practice, because levels are often grouped

into multiplets of closely spaced levels, which are more widely separated from other multiplets. Suppose to be specific that two levels, say, ϵ_n and ϵ_m , are close enough to one another that first order perturbations will push the exact level E close to or onto the unperturbed level ϵ_m . Then the $k = m$ terms in Eq. (8) are small, and that equation cannot be used.

In this case we may proceed as follows. Let us choose some energy, call it $\bar{\epsilon}$, which is close to ϵ_n and ϵ_m . It could, for example, be one of the energies ϵ_n or ϵ_m themselves, or it could be their average, etc. Then let us take the original unperturbed Hamiltonian and perturbation and rearrange them in the form,

$$H = H_0 + H_1 = H'_0 + H'_1, \quad (29)$$

where

$$H_0 = \sum_{k\alpha} \epsilon_k |k\alpha\rangle\langle k\alpha|, \quad (30)$$

$$H'_0 = \sum_{\substack{k \neq n, m \\ \alpha}} \epsilon_k |k\alpha\rangle\langle k\alpha| + \sum_{\substack{k=n, m \\ \alpha}} \bar{\epsilon} |k\alpha\rangle\langle k\alpha|, \quad (31)$$

$$H'_1 = H_1 + \sum_{\substack{k=n, m \\ \alpha}} (\epsilon_k - \bar{\epsilon}) |k\alpha\rangle\langle k\alpha|. \quad (32)$$

In effect, we have merged the nearly degenerate levels ϵ_n , ϵ_m into a single degenerate level $\bar{\epsilon}$, and thrown the correction terms into H'_1 . Then standard degenerate perturbation theory may be applied. We will call this procedure “nearly degenerate perturbation theory.”

An equivalent approach to nearly degenerate perturbation theory is to exclude both sets of terms $k = n$ and $k = m$ from the definition of R , and to proceed from there. Then R becomes the inverse of $E - H_0$ on the space orthogonal to $\mathcal{H}_n \oplus \mathcal{H}_m$.

Problems

1. Compute the shifts in the energy levels of a single-electron (hydrogen-like) atom of nuclear charge Z due to the finite size of the nucleus. Treat the nucleus as a uniform sphere of charge of radius $r_0 A^{1/3}$, where $r_0 = 1.0 \times 10^{-13}$ cm and A is the number of nucleons. Express your answer as some number of eV times some function of Z , A , and the quantum numbers of the atomic state. Only treat those atomic states for which the effect is the largest. This is called the *volume effect*. You may use

$$R_{n0}(0) = 2 \left(\frac{Z}{na_0} \right)^{3/2}, \quad (33)$$

valid in hydrogen-like atoms, where $a_0 = \hbar^2/me^2$ is the Bohr radius.

The volume effect induces a splitting between the $2s$ and $2p$ levels of hydrogen. Compare this to the Lamb shift (another splitting of the same two levels). The Lamb shift suppresses the $2p$ level relative to the $2s$ level by approximately 1.05 GHz in frequency units.

2. In this problem, set $\hbar = 1$ for simplicity. The Hamiltonian for a rigid body is

$$H = \frac{1}{2} \left(\frac{L_1^2}{I_1} + \frac{L_2^2}{I_2} + \frac{L_3^2}{I_3} \right), \quad (34)$$

where (I_1, I_2, I_3) are the principal moments of inertia and where $(L_1, L_2, L_3) = (L_x, L_y, L_z)$ are angular momentum operators satisfying the commutation relations,

$$[L_i, L_j] = i \epsilon_{ijk} L_k. \quad (35)$$

You may assume that the angular momentum takes on only integer values. The Hamiltonian (34) describes the rotational spectrum of molecules. Physically, the quantities L_i are the negatives of the components of the angular momentum with respect to the body frame.

In the case of a *spherical top*, such as methane, we have $I_1 = I_2 = I_3 = I$. The Hamiltonian is

$$H = \frac{L^2}{2I}, \quad (36)$$

and the energy levels are

$$E_\ell = \frac{\ell(\ell+1)}{2I}, \quad (37)$$

which is $(2\ell+1)$ -fold degenerate since E_ℓ is independent of m .

In the case of a *symmetric top* such as ammonia, we have $I_1 = I_2 = I_\perp \neq I_3$. The Hamiltonian is

$$H = \frac{1}{2} \left(\frac{L^2 - L_3^2}{2I_\perp} + \frac{L_3^2}{2I_3} \right), \quad (38)$$

and the energy levels are

$$E_{\ell m} = A + Bm^2, \quad (39)$$

where

$$A = \frac{\ell(\ell+1)}{2I_\perp}, \quad B = \frac{1}{2} \left(\frac{1}{I_3} - \frac{1}{I_\perp} \right), \quad (40)$$

and where m is the usual quantum number of L_z .

Now consider the case of a slightly *asymmetric top*. (Water is an example of an asymmetric top molecule.) Let

$$\frac{1}{I_1} = \frac{1+\epsilon}{I_\perp}, \quad \frac{1}{I_2} = \frac{1-\epsilon}{I_\perp}, \quad (41)$$

where ϵ is small. These equations are equivalent to defining

$$I_\perp = \frac{2I_1 I_2}{I_1 + I_2}, \quad \epsilon = \frac{I_2 - I_1}{I_1 + I_2}. \quad (42)$$

Write the Hamiltonian as $H = H_0 + \epsilon H_1$, where H_0 is the symmetric top Hamiltonian in Eq. (38).

You may find the following relations useful:

$$\langle m | L_+^2 | m' \rangle = \langle m' | L_-^2 | m \rangle^*, \quad (43a)$$

$$\langle m | L_+^2 | m' \rangle = (-1)^{m+m'} \langle -m' | L_+^2 | -m \rangle, \quad (43b)$$

but if you use Eq. (43b) you must prove it.

(a) Consider the state $m = 0$. Find the first order of perturbation theory at which the energy shift does not vanish, and compute the energy shift at that order. In addition to the abbreviations (40), use

$$C = \frac{1}{4I_{\perp}}, \quad (44)$$

and express your answer in terms of the constants A , B and C .

(b) Find the first order of perturbation theory at which the energy shifts for the $m = \pm 1$ levels do not vanish, and compute them at that order.

(c) Find the first order of perturbation theory at which the energy shifts for the $m = \pm 2$ levels do not vanish, and compute them at that order. Express your answer in terms of

$$X = \frac{\ell(\ell-1)(\ell+1)(\ell+2)}{4B}, \quad Y = \frac{(\ell-3)(\ell-2)(\ell+3)(\ell+4)}{12B}. \quad (45)$$

See also Sakurai's problem 12, p. 348. Notice the appearance of a sum over "intermediate states."

(d) What order of perturbation theory do you have to go to in order to find the first nonvanishing correction to the energy in the case of $m = \pm 3$? $m = \pm 4$?