

Chapter 11

STATIONARY STATE PERTURBATION THEORY

Often one meets a problem in quantum mechanics that can't be solved exactly, but looks very similar to a problem that can be solved exactly. For example, suppose that we have to find the energies and eigenstates of a Hamiltonian of the form

$$H = H_0 + V \quad (11-1)$$

where the eigenstates $|n\rangle$ and energies ϵ_n of H_0 are known exactly

$$H_0|n\rangle = \epsilon_n|n\rangle. \quad (11-2)$$

If V is in some sense a small correction to H_0 then we might expect that the eigenstates $|N\rangle$ of H are only slightly different from the eigenstates $|n\rangle$ of H_0 , and the energies E_n of H are only slightly different from the ϵ_n . In other words, if we put a parameter λ in front of V , so that

$$H = H_0 + \lambda V \quad (11-3)$$

then we expect that as the coupling constant λ is varied from zero to one each eigenstate $|n\rangle$ will smoothly become an eigenstate $|N\rangle$ of $H_0 + V$ and the energy ϵ_n will smoothly become the energy of the state $|N\rangle$.

Let us then look for expansions of the eigenstates and energies of $H_0 + \lambda V$ in powers of λ [eventually we shall set $\lambda = 1$, but for now it is a convenient way of keeping track of powers of V]:

$$|N\rangle = |n\rangle + \lambda|N^{(1)}\rangle + \lambda^2|N^{(2)}\rangle + \dots \quad (11-4)$$

$$E_n = \epsilon_n + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \quad (11-5)$$

It should be emphasized right away that the existence of such expansions is a rather strong assumption. For example, the energy of the Cooper pair, Eq. (8-29), can certainly not be expanded in powers of v_0 , the interaction strength. The bound states of a weak attractive potential never come out of doing perturbation theory on free particle states. They can't: expanding the states, say, in a power series implies that the physics with a small positive V is only slightly different from the physics with a small negative V . But this is certainly not the case for a bound state; a weak attractive potential can have a bound state, but a weak repulsive potential can't — a much different situation. Look, for example, at Eq. (4-65) for the bound state energy of a shallow square well:

$$E = \frac{-mV^2 a^2}{2\hbar^2}.$$

This is definitely not the first (or second) term in a power series in V ; were that the case, this formula would have to give us the correct result for either sign of V , but a state with $E < 0$ for a repulsive potential is clearly impossible. With this warning we return to the expansions.

Let us assume that the eigenstates of H_0 are normalized to 1, $\langle n|n \rangle = 1$, and let us choose the normalization of $|N\rangle$ so that

$$\langle n|N \rangle = 1. \quad \Rightarrow \langle N|N \rangle \neq 1 \text{ will evaluate later} \quad (11-6)$$

Therefore

$$\langle n|N \rangle = 1 = \langle n|n \rangle + \lambda \langle n|N^{(1)} \rangle + \lambda^2 \langle n|N^{(2)} \rangle + \dots$$

The coefficients in this equation of each power of λ must vanish individually, and therefore

$$\langle n|N^{(i)} \rangle = 0, \quad i = 1, 2, \dots \quad (11-7)$$

To find the coefficients in the power series for $|N\rangle$ and E_n we put the expansions (11-4) and (11-5) into the Schrödinger equation

$$(H_0 + \lambda V)|N\rangle = E_n|N\rangle \quad (11-8)$$

and compare the coefficients of powers of λ on both sides of (11-8). This yields the following equations:

$$H_0|n\rangle = \epsilon_n|n\rangle \quad (11-9)$$

as the coefficient of λ^0 . The λ^1 term is

$$H_0|N^{(1)}\rangle + V|n\rangle = \varepsilon_n|N^{(1)}\rangle + E_n^{(1)}|n\rangle \quad (11-10)$$

and in general for λ^k ($k > 1$),

$$H_0|N^{(k)}\rangle + V|N^{(k-1)}\rangle = \varepsilon_n|N^{(k)}\rangle + E_n^{(1)}|N^{(k-1)}\rangle + \dots + E_n^{(k)}|n\rangle. \quad (11-11)$$

Taking the scalar product of both sides of (11-10) with $\langle n|$ gives

$$\langle n|H_0|N^{(1)}\rangle + \langle n|V|n\rangle = \varepsilon_n \langle n|N^{(1)}\rangle + E_n^{(1)}, \quad (11-12)$$

since $\langle n|n\rangle = 1$. Using (11-2) in the first term on the left-hand side of (11-12) we find

$$E_n^{(1)} = \langle n|V|n\rangle. \quad (11-13)$$

Thus to first order (in λ , and therefore V), the energy shift is

$$E_n - \varepsilon_n = \lambda \langle n|V|n\rangle, \quad (11-14)$$

which is just the expectation value of the perturbation λV .

Taking the scalar product of both sides of (11-11) with $\langle n|$ and using (11-7) we find

$$E_n^{(k)} = \langle n|V|N^{(k-1)}\rangle. \quad (11-15)$$

Thus once we know the change in the state to a certain order, we can find the energy change in the next order from (11-15). The remaining problem is to find the change in the state $|n\rangle$ due to the perturbation. Notice that if we multiply both sides of (11-15) by λ^k and sum over k from one to infinity we find the simple result

$$E_n = \varepsilon_n + \langle n|V|N\rangle. \quad (11-16)$$

The k^{th} -order change in the state $|N^{(k)}\rangle$ can be expanded in terms of the complete set of eigenstates of H_0 :

$$|N^{(k)}\rangle = \sum'_m |m\rangle \langle m|N^{(k)}\rangle, \quad k = 1, 2, \dots \quad (11-17)$$

where the prime on the sum means that, because of the orthogonality relation (11-7), we shouldn't include the state $|n\rangle$ in the sum. Now to find the coefficient $\langle m|N^{(i)}\rangle$ we take the scalar product of both sides of Eq. (11-11) with $\langle m|$. Thus

$$\langle m|H_0|N^{(k)}\rangle + \langle m|V|N^{(k-1)}\rangle = \varepsilon_n \langle m|N^{(k)}\rangle + \dots + E_n^{(k-1)} \langle m|N^{(1)}\rangle.$$

Similar to eq 7 then + to 13, the same.

However, $\langle m | H_0 = \epsilon_m \langle m |$, so that if $\epsilon_m \neq \epsilon_n$,

$$\langle m | N^{(k)} \rangle = \frac{1}{\epsilon_n - \epsilon_m} \left(\langle m | V | N^{(k-1)} \rangle - E^{(1)} \langle m | N^{(k-1)} \rangle - \dots - E_n^{(k-1)} \langle m | N^{(1)} \rangle \right). \quad (11-18)$$

This formula enables us to find the k^{th} -order correction to the state in terms of lower-order corrections to $|N\rangle$ and ϵ_n , as long as the state $|n\rangle$ is nondegenerate. Later we shall consider what one must do if the level $|n\rangle$ being perturbed is degenerate.

Now let us examine the first few orders. Letting $k = 1$ in (11-18) we find

$$\langle m | N^{(1)} \rangle = \frac{1}{\epsilon_n - \epsilon_m} \langle m | V | n \rangle \quad (11-19)$$

since $|N^{(0)}\rangle = |n\rangle$ and $\langle m | n \rangle = 0$. Hence to *first order* in λ (see (1-7))

$$|N\rangle = |n\rangle + \lambda \sum_m' |m\rangle \frac{\langle m | V | n \rangle}{\epsilon_n - \epsilon_m} \quad (11-20)$$

and

$$E_n = \epsilon_n + \lambda \langle n | V | n \rangle. \quad (11-21)$$

[One may set $\lambda = 1$ in these formulas at this point; they clearly are first order in V .]

Now that we have found the first-order change in the state, we can find the second-order energy immediately from (11-15). Thus

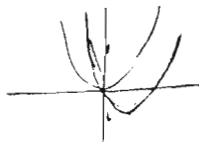
$$E_n^{(2)} = \sum_m' \langle n | V | m \rangle \frac{1}{\epsilon_n - \epsilon_m} \langle m | V | n \rangle = \sum_m' \frac{|\langle n | V | m \rangle|^2}{\epsilon_n - \epsilon_m}. \quad (11-22)$$

Notice that if $|n\rangle$ is the ground state of H_0 , then $\epsilon_m - \epsilon_n > 0$, and therefore $E_n^{(2)}$ is negative. We find from (11-18) that the second-order term $|N^{(2)}\rangle$ is

$$\sum_m' \sum_k' |m\rangle \frac{\langle m | V | k \rangle \langle k | V | n \rangle}{(\epsilon_n - \epsilon_k)(\epsilon_n - \epsilon_m)} - \sum_m' |m\rangle \frac{\langle m | V | n \rangle \langle n | V | n \rangle}{(\epsilon_n - \epsilon_m)^2}. \quad (11-23)$$

Consider as an example a one-dimensional harmonic oscillator perturbed by a constant force

$$V = -Fx. \quad (11-24)$$



Then the only nonvanishing matrix elements of V are

$$\langle n|V|n+1\rangle = -F\langle n|x|n+1\rangle = -F\left|\frac{\hbar(n+1)}{2m\omega}\right|^{1/2} \quad (11-25)$$

and

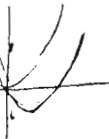
$$\langle n|V|n-1\rangle = -F\left|\frac{\hbar n}{2m\omega}\right|^{1/2}. \quad (11-26)$$

The first-order energy correction $E_n^{(1)}$ vanishes since $\langle n|x|n\rangle = 0$. The second-order change in the energy is

$$E_n^{(2)} = \sum_m' \frac{|\langle n|V|m\rangle|^2}{\epsilon_n - \epsilon_m} = \frac{|\langle n|V|n+1\rangle|^2}{-\hbar\omega} + \frac{|\langle n|V|n-1\rangle|^2}{\hbar\omega} = \frac{-F^2}{2m\omega^2}. \quad (11-27)$$

The energy of each state decreases by the same amount.

We could have learned this by a more direct argument, since



$$H = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2} - Fx = \frac{p^2}{2m} + \frac{m\omega^2}{2} \left(x - \frac{F}{m\omega^2}\right)^2 - \frac{F^2}{2m\omega^2},$$

which is again a Hamiltonian for simple harmonic motion, now centered about the point $F/m\omega^2$. The frequencies are the same and the only change in the energy is the constant term (11-27). One expects then that the states are just the old states translated in space by the distance $F/m\omega^2$, and are therefore given by¹

$$|\bar{N}\rangle = e^{-ipF/m\omega^2\hbar}|n\rangle, \quad (11-28)$$

where p is the momentum operator. It is left as exercise to show from the perturbation theory that

$$|\bar{N}^{(1)}\rangle = -\frac{iF}{\hbar m\omega^2} p|n\rangle$$

$$|\bar{N}^{(2)}\rangle = -\left(\frac{F}{\hbar m\omega^2}\right)^2 p^2|n\rangle, \quad (11-29)$$

etc.

THE WAVE FUNCTION RENORMALIZATION CONSTANT

We have constructed the perturbed state $|\bar{N}\rangle$ to have the normalization $\langle n|\bar{N}\rangle = 1$. If we want the perturbed state to be normalized to

¹Note that the perturbed state $|\bar{N}\rangle$ in (11-28) is already normalized to one; this is indicated by the bar. See Eq. (11-31).

one, we must multiply $|N\rangle$ by

$$\langle N|N\rangle^{-1/2} \equiv Z^{1/2}; \quad (11-30)$$

The state

$$|\bar{N}\rangle = Z^{1/2}|N\rangle \quad (11-31)$$

obeys

$$\langle \bar{N}|\bar{N}\rangle = 1. \quad (11-32)$$

The quantity Z is known as the *wave function renormalization constant*. Multiplying both sides of (11-31) by $\langle n|$ we see that

$$Z^{1/2} = \langle n|\bar{N}\rangle. \quad (11-33)$$

Let us calculate Z to second order. Using (11-6) we find

$$\begin{aligned} \langle N|N\rangle &= (\langle n| + \lambda \langle N^{(1)}| + \lambda^2 \langle N^{(2)}|)(|n\rangle + \lambda |N^{(1)}\rangle + \lambda^2 |N^{(2)}\rangle) \\ &= 1 + \lambda^2 \langle N^{(1)}|N^{(1)}\rangle + \dots \end{aligned}$$

Thus

$$\langle N|N\rangle = 1 + \lambda^2 \sum_m \frac{|\langle m|V|n\rangle|^2}{(\epsilon_n - \epsilon_m)^2}. \quad (11-34)$$

We see therefore that the state $|N\rangle$ is, to first order, normalized to 1, with the first correction occurring in second order. To this order

$$\begin{aligned} Z &= 1 - \lambda^2 \sum_m \frac{\langle m|V|n\rangle^2}{(\epsilon_n - \epsilon_m)^2} \\ &= \frac{\partial}{\partial \epsilon_n} \left(\epsilon_n + \lambda \langle n|V|n\rangle + \lambda^2 \sum_m \frac{|\langle m|V|n\rangle|^2}{\epsilon_n - \epsilon_m} \right) = \frac{\partial E_n}{\partial \epsilon_n}. \end{aligned} \quad (11-35)$$

This result is true to all orders: if the system is in the eigenstate $|N\rangle$, the probability $Z = |\langle n|\bar{N}\rangle|^2$ of observing it in the unperturbed state $|n\rangle$ is given by the partial derivative of the perturbed energy with respect to the unperturbed energy, keeping fixed the matrix elements of the perturbation as well as the other ϵ_m .

DEGENERATE PERTURBATION THEORY

It is clear from Eqs. (11-20), (11-22), and (11-23) that the above formulation of perturbation theory is essentially an expansion in quantities like $\lambda \langle n|V|m \rangle / (\epsilon_n - \epsilon_m)$. We may expect it to be more rapidly converging the smaller are the matrix elements of V compared with the level spacing of the unperturbed system. On the other hand if there are any states for which $\epsilon_n = \epsilon_m$ but $\langle n|V|m \rangle \neq 0$, then the theory breaks down. Let us consider what must be done in this case.

Suppose that we have a group of states

$$|n_a\rangle, |n_b\rangle, \dots, |n_k\rangle$$

that are degenerate states of the unperturbed Hamiltonian H_0 :

$$H_0|n_i\rangle = \epsilon_n|n_i\rangle \quad \text{for } i = a, b, c, \dots, k. \quad (11-36)$$

Then if $\langle n_a|V|n_b\rangle$ is nonzero for $a \neq b$, the previous perturbation method will fail. However, any linear combination of the states $|n_a\rangle, |n_b\rangle, \dots, |n_k\rangle$ is also an eigenstate with the same energy ϵ_n . Thus if we can choose a set of k orthogonal states

$$|n_\alpha\rangle = \sum_{i=a}^k C_{\alpha i} |n_i\rangle \quad (11-37)$$

such that

$$\langle n_\alpha|V|n_\beta\rangle = 0 \quad \text{if } \alpha \neq \beta, \quad (11-38)$$

we can use the perturbation procedure as given, for then vanishing energy denominators will always be accompanied by vanishing numerators and we will have no trouble. The correct choice of basis states to use in doing the perturbation expansion is therefore the one that diagonalizes V within each group of degenerate states, i.e., $\langle n_\alpha|V|n_\beta\rangle = 0$ if $\alpha \neq \beta$ and $\epsilon_{n_\alpha} = \epsilon_{n_\beta}$.

Should we be interested in the perturbation of only one group of degenerate states of H_0 with energy ϵ_n , then it is only necessary to diagonalize V within that one group of states. This is because all the energy denominators that occur in the perturbation expansion are energy differences between ϵ_n and other states, and thus other degeneracies of H_0 don't lead to vanishing denominators.

The problem of diagonalizing V within a group of states $|n_a\rangle, |n_b\rangle, \dots$ is just that of finding the eigenvector of the $k \times k$ matrix

$$\begin{pmatrix} \langle n_a | V | n_a \rangle & \langle n_a | V | n_b \rangle & \langle n_a | V | n_c \rangle & \dots \\ \langle n_b | V | n_a \rangle & \langle n_b | V | n_b \rangle & \dots & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix} \quad (11-39)$$

We shall now show that if the $C_{\alpha i}$ are the components of the eigenvectors \mathbf{C}_α of this matrix, then (11-38) is satisfied. To see this, suppose that

$$\sum_i \langle n_j | V | n_i \rangle C_{\alpha i} = E_{n_\alpha}^{(1)} C_{\alpha j}, \quad (11-40)$$

where $E_{n_\alpha}^{(1)}$ is the name of the eigenvalue, and that C_α is normalized to one:

$$\sum_i |C_{\alpha i}|^2 = 1. \quad (11-41)$$

Multiplying on the left by $C_{\beta j}^*$, the components of another eigenvector of unit length, we have

$$\left(\sum_j C_{\beta j}^* \langle n_j | \right) V \left(\sum_i C_{\alpha i} | n_i \rangle \right) = E_{n_\alpha}^{(1)} \sum_j C_{\beta j}^* C_{\alpha j}.$$

However,

$$\sum_j C_{\beta j}^* C_{\alpha j} = \delta_{\alpha\beta} \sum_j C_{\beta j}^* C_{\beta j} = \delta_{\alpha\beta} \quad (11-42)$$

since the eigenvectors of the $k \times k$ Hermitian matrix $\langle n_a | V | n_b \rangle$ can be taken to form an orthonormal set. Thus the vectors

$$|n_\alpha\rangle = \sum_i C_{\alpha i} |n_i\rangle \quad \downarrow \text{pg 106 off Chan.} \quad (11-43)$$

obey

$$\langle n_\beta | V | n_\alpha \rangle = E_{n_\alpha}^{(1)} \delta_{\alpha\beta}. \quad (11-44)$$

The eigenvalue $E_{n_\alpha}^{(1)}$ is clearly λ^{-1} times the first-order energy shift of the state $|n_\alpha\rangle$.

Thus the group of states $|n_a\rangle, |n_b\rangle, \dots$ in the presence of the perturbation splits into k states $|N_\alpha\rangle, |N_\beta\rangle, \dots$ which are given in first order by

$$|N_\alpha\rangle = |n_\alpha\rangle + \sum'_m \frac{|m\rangle \langle m|V|n_\alpha\rangle}{\epsilon_n - \epsilon_m} \quad (11-45)$$

where the prime on the sum over m means that the sum runs over all states *except* the k states $|n_\alpha\rangle, |n_\beta\rangle, \dots$. The energy shift to second order is

$$E_{n\alpha} = \epsilon_n + \lambda \langle n_\alpha | V | n_\alpha \rangle + \lambda^2 \sum'_m \frac{|\langle m | V | n_\alpha \rangle|^2}{\epsilon_n - \epsilon_m} \quad (11-46)$$

where $\langle n_\alpha | V | n_\alpha \rangle$ is the eigenvalue $E_{n\alpha}^{(1)}$ of the matrix $\langle n_a | V | n_b \rangle$.

As an example let us consider the splitting by a uniform electric field \mathcal{E} , of the fourfold degenerate $n = 2$ levels of the hydrogen atom. This phenomenon is known as the *Stark effect*. The four $n = 2$ states are

$$|2S_0\rangle, \quad |2P_1\rangle, \quad |2P_0\rangle, \quad |2P_{-1}\rangle.$$

Taking the field to be in the z direction, the perturbation λV is $e\mathcal{E}z$. First of all we notice that the matrix elements of λV between states with different eigenvalues of L_z all vanish. This is because $e\mathcal{E}z$ commutes with L_z . Thus, for example

$$\begin{aligned} 0 &= \langle 2P_{-1} | e\mathcal{E}z, L_z | 2P_1 \rangle = \langle 2P_{-1} | e\mathcal{E}z (L_z | 2P_1 \rangle) - \langle \langle 2P_{-1} | L_z \rangle e\mathcal{E}z | 2P_1 \rangle \\ & \quad [L_z, z] = 0 \\ & \quad = 2\hbar \langle 2P_{-1} | e\mathcal{E}z | 2P_1 \rangle \end{aligned}$$

so that

$$\langle 2P_{-1} | e\mathcal{E}z | 2P_1 \rangle = 0.$$

\Rightarrow if $[V, A] = 0$
 $\Rightarrow \forall A$ have same set

This is a quite general rule: if the perturbation commutes with a constant of the motion, A , of the unperturbed Hamiltonian, then matrix elements of the perturbation between eigenstates of A with different eigenvalues must vanish. This rule, an example of a *selection rule*, often simplifies the problem of selecting the correct linear combination of degenerate states with which to do the perturbation expansion. The only nonvanishing off-diagonal matrix elements $\langle n_a | V | n_b \rangle$ are $\langle 2S_0 | e\mathcal{E}z | 2P_0 \rangle$ and $\langle 2P_0 | e\mathcal{E}z | 2S_0 \rangle$. We must only worry about the degeneracy between the two $m = 0$ states.

Because the hydrogen atom is invariant under the parity operation: $\mathbf{r} \rightarrow -\mathbf{r}$, the diagonal matrix elements of $e\mathcal{E}z$ are zero; since $|\psi_{n\ell m}(\mathbf{r})|^2 = |\psi_{n\ell m}(-\mathbf{r})|^2$ for unperturbed hydrogen atom wave functions, the electron in the state $|n\ell m\rangle$ is as likely to be found at \mathbf{r} as at $-\mathbf{r}$. Thus $\langle n\ell m | z | n\ell m \rangle$, the expectation value of z , must vanish.

We must therefore find the eigenvalues of the matrix

$$\begin{pmatrix} 0 & \langle 2P_0 | e\mathcal{E}z | 2S_0 \rangle \\ \langle 2S_0 | e\mathcal{E}z | 2P_0 \rangle & 0 \end{pmatrix}. \quad (11-47)$$

Since

$$\langle 2P_0 | z | 2S_0 \rangle = \langle 2S_0 | z | 2P_0 \rangle = -3a_0, \quad (11-48)$$

the eigenvectors are $\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix}$ with eigenvalues $\mp 3a_0$. Hence the state which in zero order is $(1/\sqrt{2})(|2S_0\rangle + |2P_0\rangle)$ will have a first-order energy shift $-3e\mathcal{E}a_0$, while the state which in zero order is $(1/\sqrt{2})(|2S_0\rangle - |2P_0\rangle)$ will have a first-order energy shift $+3e\mathcal{E}a_0$. In order of magnitude the energy shift is a dimensionless factor $\mathcal{E}/(e/a_0^2)$ times the spacing of the low-lying hydrogen levels; the "atomic field" e/a_0^2 is the electric field of a proton at one Bohr radius;

$$\frac{e}{a_0^2} = 5.15 \times 10^9 \text{ volts/cm.} \quad \frac{V}{\Delta E} \sim \frac{e\mathcal{E}a_0}{e^2/a_0} = \frac{\mathcal{E}}{e/a_0^2} \quad (11-49)$$

Thus the perturbation expansion converges rapidly for everyday electric field strengths.

If the atom is originally, for example, in a $|2S_0\rangle$ state before the field is turned on, then in the presence of the electric field this state becomes a linear combination of the two perturbed eigenstates that in lowest order are

$$\frac{1}{\sqrt{2}}(|2S_0\rangle + |2P_0\rangle), \quad \frac{1}{\sqrt{2}}(|2S_0\rangle - |2P_0\rangle).$$

If we measure the energy of the perturbed $|2S_0\rangle$ state we find either

$$-\frac{e^2}{2a_0} \left(1 + \frac{6\mathcal{E}}{e/a_0^2} \right) \quad \text{or} \quad -\frac{e^2}{2a_0} \left(1 - \frac{6\mathcal{E}}{e/a_0^2} \right)$$

The shifts are $\langle n_0 | V | n_0 \rangle$ values

with equal probability.

① Notice that in the nondegenerate case if the diagonal matrix element $\langle n | V | n \rangle$ vanishes then the first energy shift is second order; however, as we see in the Stark effect one can still get a first-order energy shift in the degenerate case even if the diagonal matrix elements of V vanish in the original basis.

VAN DER WAALS INTERACTION

An important application of perturbation theory is the derivation of the energy of interaction of two widely separated atoms. To see

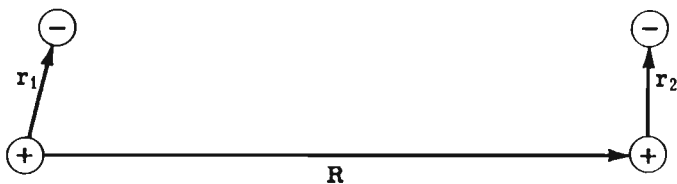


Fig. 11-1

how this works let's consider the interaction between two hydrogen atoms, treating the two protons as fixed point charges separated by a vector \mathbf{R} . Let \mathbf{r}_1 be the vector from the first proton to its electron and \mathbf{r}_2 the vector from the second proton to its electron [Fig. 11-1]. Then the interaction between the two atoms is the sum of the various Coulomb interactions between the charges on the first atom and the second atom:

$$V = e^2 \left[\frac{1}{R} + \frac{1}{|\mathbf{R} + \mathbf{r}_2 - \mathbf{r}_1|} - \frac{1}{|\mathbf{R} + \mathbf{r}_2|} - \frac{1}{|\mathbf{R} - \mathbf{r}_1|} \right]. \quad (11-50)$$

If R is many Bohr radii we may expand the denominators in (11-50) in powers of \mathbf{r}_1/R and \mathbf{r}_2/R . The first nonvanishing terms are second order:

$$V = -e^2 (\mathbf{r}_1 \cdot \nabla) (\mathbf{r}_2 \cdot \nabla) \frac{1}{R} = e^2 \left[\frac{\mathbf{r}_1 \cdot \mathbf{r}_2}{R^3} - \frac{3(\mathbf{r}_1 \cdot \mathbf{R})(\mathbf{r}_2 \cdot \mathbf{R})}{R^5} \right]. \quad (11-51)$$

Thus, at large separation the interaction between the atoms is simply that between two dipoles $e\mathbf{r}_1$ and $e\mathbf{r}_2$ separated by \mathbf{R} . If we choose the z axis along \mathbf{R} then the interaction operator (11-51) becomes

$$V = \frac{e^2}{R^3} (x_1 x_2 + y_1 y_2 - 2z_1 z_2). \quad (11-52)$$

Suppose that in the absence of this interaction, atom 1 is in state $|n_1\rangle$ and atom 2 is in state $|n_2\rangle$. The unperturbed energy of the two atoms is $\epsilon_{n_1} + \epsilon_{n_2}$. To find the interaction energy of the two atoms we calculate the energy of two atoms including V by perturbation theory. This energy depends on R , and hence behaves as an effective potential energy of interaction. To first order

$$E(R) = \epsilon_{n_1} + \epsilon_{n_2} + \langle n_1 n_2 | V(R) | n_1 n_2 \rangle. \quad (11-53)$$

what coord(s) is matrix element over.
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Now from (11-52) the diagonal matrix element of V is

$$\langle n_1 n_2 | V(R) | n_1 n_2 \rangle = \frac{e^2}{R^3} \left(\langle n_1 | x_1 | n_1 \rangle \langle n_2 | x_2 | n_2 \rangle + \langle n_1 | y_1 | n_1 \rangle \langle n_2 | y_2 | n_2 \rangle - 2 \langle n_1 | z_1 | n_1 \rangle \langle n_2 | z_2 | n_2 \rangle \right), \quad (11-54)$$

since the wave function of the state $|n_1 n_2\rangle$ is a simple product of the wave functions of the states $|n_1\rangle$ and $|n_2\rangle$. If either of the atoms is in its ground state then from the reflection symmetry of the ground state wave function, (11-54) vanishes and the first correction to the energy appears in second order. On the other hand, if both of the atoms are in degenerate states we must carry out the necessary diagonalization procedure for V ; then we find a nonvanishing interaction energy in first order. This interaction energy behaves as $1/R^3$.

To second order, assuming $|n_1\rangle$ and $|n_2\rangle$ to be nondegenerate,

$$E^{(2)}(R) = \frac{e^4}{R^6} \sum_{m_1 m_2}' \frac{|\langle n_1 n_2 | (x_1 x_2 + y_1 y_2 - 2z_1 z_2) | m_1 m_2 \rangle|^2}{\epsilon_{n_1} + \epsilon_{n_2} - \epsilon_{m_1} - \epsilon_{m_2}}. \quad (11-55)$$

The state with $m_1 = n_1$ and $m_2 = n_2$ is excluded from the sum. We see two immediate features of this interaction energy; first, if both atoms are in their ground states then $E^{(2)}(R)$ is negative. Furthermore, the interaction energy falls off as the inverse sixth power of the separation of the atoms. Let us write

$$\zeta = \frac{e^2}{a_0^5} \sum_{m_1 m_2}' \frac{|\langle n_1 n_2 | (x_1 x_2 + y_1 y_2 - 2z_1 z_2) | m_1 m_2 \rangle|^2}{\epsilon_{m_1} + \epsilon_{m_2} - \epsilon_{n_1} - \epsilon_{n_2}}; \quad (11-56)$$

ζ is a dimensionless constant whose value, from detailed calculations for the case of two hydrogen atoms in their ground states, is 6.5.

The total energy of the two atoms is thus

$$E(R) = \epsilon_{n_1} + \epsilon_{n_2} - \frac{e^2}{a_0} \left(\frac{a_0}{R} \right)^6 \zeta; \quad (11-57)$$

the second-order energy acts as an effective potential energy for the interaction between two widely separated hydrogen atoms in their ground states. This effective potential is known as a *van der Waals* interaction. The physics behind this interaction is that even though a hydrogen atom in its ground state has no permanent electric dipole moment ($\langle -e\mathbf{r} \rangle = 0$), the presence of a second atom in the vicinity of this first atom induces a dipole moment in the first whose components are proportional to the dipole moment operator of the

second atom times R^{-3} . The van der Waals interaction is essentially the interaction ($\sim R^{-3}$) of this induced dipole moment with the dipole moment operator of the second atom (and vice versa). [The interaction is certainly not that between the induced dipole moment of the first atom ($\sim R^{-3}$) and the induced dipole moment of the second atom ($\sim R^{-3}$) since that goes as R^{-9} .] Atoms in their ground states attract each other; however atoms in excited states can either attract or repel each other.

The interaction at short distances is very complicated, because it is then necessary to take into account the exclusion principle between the electrons on the two atoms. Noble gas atoms — helium, argon, etc. — tend to repel each other at short distances because the electrons refuse to overlap each other. This repulsion leads to an energy behaving roughly as R^{-12} . The combination of a repulsive R^{-12} potential plus an attractive R^{-6} van der Waals potential is known as a *6-12 potential*. We shall study this short ranged interaction when we look at molecules.

ALMOST DEGENERATE PERTURBATION THEORY

Let us consider how to do perturbation theory when two energy levels of H_0 are very closely spaced. This is a troublesome case because the perturbation theory expands in quantities like $\langle n|V|m\rangle/(\epsilon_n - \epsilon_m)$ and if $|\epsilon_n - \epsilon_m|$ is ever small compared with $|\langle n|V|m\rangle|$ then the expansions for the effects of the perturbation on the states $|n\rangle$ and $|m\rangle$ will converge very slowly.

Suppose for simplicity that only two eigenstates $|n\rangle$ and $|m\rangle$ of H_0 are very closely spaced in energy. To develop a more rapidly convergent perturbation expansion we can proceed in two steps, analogous to the procedure for degenerate states. First we handle the effects of the matrix elements of the perturbation, $\langle n|V|n\rangle$, $\langle m|V|m\rangle$, $\langle n|V|m\rangle$, and $\langle m|V|n\rangle$ exactly, and then treat the rest of the perturbation by ordinary perturbation theory. Let us therefore write V as

$$V = \sum_{ij} |i\rangle \langle i|V|j\rangle \langle j| \quad (11-58)$$

where the sums are over eigenstates of H_0 . Then let us separate out the part of V referring to $|n\rangle$ and $|m\rangle$ alone by writing

$$V = V_1 + V_2$$

$k=2$

pg 228 eq (11-23)

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$$\langle m | N^{(2)} \rangle = \frac{1}{\epsilon_n - \epsilon_m} \left(\langle m | V | N^{(1)} \rangle - E^{(1)} \langle m | N^{(1)} \rangle \right) \quad (11-18)$$

$$E^{(1)} = \langle n | V | n \rangle \quad | N^{(1)} \rangle = \sum_m \left(\frac{1}{\epsilon_n - \epsilon_m} \right) \langle m | V | n \rangle | m \rangle$$

↓ or write this as

$$\langle m | N^{(1)} \rangle = \frac{1}{\epsilon_n - \epsilon_m} \langle m | V | n \rangle \quad | N^{(1)} \rangle = \sum_k \frac{1}{\epsilon_n - \epsilon_k} \langle k | V | n \rangle | k \rangle$$

$$| N^{(2)} \rangle = \sum'_m | m \rangle \langle m | N^{(2)} \rangle$$

$$= \sum_m | m \rangle \frac{1}{\epsilon_n - \epsilon_m} \left(\langle m | V | N^{(1)} \rangle - E^{(1)} \langle m | N^{(1)} \rangle \right)$$

$$| N^{(2)} \rangle = \sum_m | m \rangle \sum_k \frac{\langle m | V | k \rangle \langle k | V | n \rangle}{(\epsilon_n - \epsilon_m)(\epsilon_n - \epsilon_k)} - \sum_m \frac{\langle n | V | n \rangle \langle m | V | n \rangle}{(\epsilon_n - \epsilon_m)(\epsilon_n - \epsilon_m)}$$

Degenerate P.T.

Have states $|n_i\rangle$ $i=1, \dots, k$

that are degenerate states of H_0

$$H_0 |n_i\rangle = E_n |n_i\rangle \quad n=1, \dots, k$$

$$|n_\alpha\rangle = \sum_{i=1}^k C_\alpha^i |n_i\rangle \quad \text{such that } \langle n_\alpha | V | n_\beta \rangle = 0 \quad \alpha \neq \beta$$

This means we need to diagonalize

$$\begin{pmatrix} \langle n_1 | V | n_1 \rangle & \langle n_1 | V | n_2 \rangle & \dots & \langle n_1 | V | n_k \rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle n_k | V | n_1 \rangle & \langle n_k | V | n_2 \rangle & \dots & \langle n_k | V | n_k \rangle \end{pmatrix}$$

Let us suppose that $\underline{C}_\alpha = (C_\alpha^1, \dots, C_\alpha^k)^T$ does just that.
This means j 'th row

$$\sum_i \langle n_j | V | n_i \rangle C_\alpha^i = E_{n_\alpha} C_\alpha^j$$

that is, if we left mult. by $\underline{C}_\beta = (C_\beta^1, \dots, C_\beta^k)$

$$\sum_j \sum_i C_\beta^j \langle n_j | V | n_i \rangle C_\alpha^i = E_{n_\alpha} \sum_j C_\beta^j C_\alpha^j = E_{n_\alpha} \underline{C}_\beta^T \underline{C}_\alpha$$

If we organize the \underline{C}_α into a matrix

$$\begin{pmatrix} \underline{C}_1 & \underline{C}_2 & \dots & \underline{C}_k \end{pmatrix}^T = \begin{pmatrix} C_1^1 & C_2^1 & \dots & C_k^1 \\ C_1^2 & C_2^2 & \dots & C_k^2 \\ \vdots & \vdots & \ddots & \vdots \\ C_1^k & C_2^k & \dots & C_k^k \end{pmatrix} = \underline{C}^T$$

$$\underline{C}^T V \underline{C} = \sum_j \sum_i C_\beta^j \langle n_j | V | n_i \rangle C_\alpha^i = E_{n_\alpha} \underline{C}_\beta^T \underline{C}_\alpha$$

$$\underline{C}^T V \underline{C} = \underline{E} \underline{I} \rightarrow \begin{pmatrix} E_1 & & 0 \\ & E_2 & \\ 0 & & \ddots \end{pmatrix}$$

$$|N_\alpha\rangle = |n_\alpha\rangle + \sum'_m \frac{|m\rangle \langle m|V|n_\alpha\rangle}{\epsilon_n - \epsilon_m}$$

and ' excludes terms in m that are the k states $|n_\alpha\rangle, |n_\beta\rangle, \dots$ because the $|n_\alpha\rangle$ states diagonalize V i.e.

$$\langle n_\beta|V|n_\alpha\rangle = 0$$

Note: remainder

$$|n_\alpha\rangle = \sum_i C_\alpha^i |n_i\rangle$$

$$\langle n_\beta|n_\alpha\rangle = \delta_{\alpha\beta}$$

$$\langle n_\beta| = \sum_j C_\beta^{*j} \langle n_j|$$

$$= \sum_j C_\beta^{*j} \left(\sum_i \langle n_j|V|n_i\rangle C_\alpha^i \right) = \sum_j C_\beta^{*j} \epsilon_n \sum_i C_\alpha^i C_\alpha^i = \epsilon_n \sum_j C_\beta^{*j} C_\alpha^j$$

so

$$\langle n_\alpha|V|n_\beta\rangle = \sum_j \sum_i C_\beta^{*j} \langle n_j|V|n_i\rangle C_\alpha^i = 0 \text{ for } \alpha \neq \beta$$

And correction is $E_{n\alpha}^{(2)} = \langle n_\alpha|V|N_\alpha^{(1)}\rangle$ to $N_\alpha^{(1)}$ from above.

$$E_{n\alpha} = \epsilon_n + \underbrace{\langle n_\alpha|V|n_\alpha\rangle}_{E_{n\alpha}^{(1)}} + \sum'_m \frac{|\langle m|V|n_\alpha\rangle|^2}{\epsilon_n - \epsilon_m}$$

Stark effect:

$$n=2 \quad \underbrace{l=0 \quad m=0}_1 \quad \underbrace{l=1 \quad m=-1, 0, 1}_3$$

$n^2 = 2^2 = 4$ degenerate states

$$n=2 \quad l=0 \quad m=0 \equiv |2S_0\rangle \equiv |00\rangle$$

$$n=2 \quad l=1 \quad m=1, 0, -1 \equiv |2P_1\rangle, |2P_0\rangle, |2P_{-1}\rangle \equiv |11\rangle, |10\rangle, |1-1\rangle$$

Write 4x4 $\begin{pmatrix} \langle 00|V|00\rangle & \langle 00|V|11\rangle & \dots \\ \vdots & & \end{pmatrix}$

Parity operation on Hydrogen atom

The parity operator P is defined as

$$P \psi(x, y, z) = \psi(-x, -y, -z)$$

$$\text{or } P \psi(\underline{r}) = \psi(-\underline{r})$$

recall that eigenvalues of P operator are ± 1

And this means its eigenfunctions are either even (+1) or odd (-1)

$$\psi_e(-\underline{r}) = \psi_e(\underline{r}) \quad \text{even}$$

$$\psi_o(-\underline{r}) = -\psi_o(\underline{r}) \quad \text{odd}$$

Consider $[P, H]$. If $[P, H] = 0$ we can classify eigenfunctions of H as even or odd.

$$[P, H] = [P, K] + [P, V]$$

$$[P, K] \psi = ?$$

$$PK\psi = P \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x, y, z) = \left(\frac{\partial^2}{\partial(-x)\partial(-x)} + - + - \right) \psi(-x, -y, -z)$$

$$= \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(-x, -y, -z) = K P \psi(x, y, z)$$

$$\therefore [P, K] = 0$$

$$[P, V] = ?$$

$$P V \psi = V(-x, -y, -z) \psi(-x, -y, -z)$$

if PE is even function of x, y, z , then

$$V(-x, -y, -z) = V(x, y, z) \text{ and}$$

$$\Rightarrow V(x, y, z) P \psi, \text{ so } [P, V] = 0$$

$$[P, V] = 0$$

For H atom $V = V(r) = V(\sqrt{x^2 + y^2 + z^2})$ so even.

$$\therefore [P, H] = 0$$

The eigenvalue - eigenvector problem is

$$\underline{V} \underline{C}_\alpha = E_\alpha \underline{C}_\alpha$$

or

$$(\underline{V} - E_\alpha \underline{1}) \underline{C}_\alpha = 0$$

For solutions of these linear (in the C_α^i coefficients) equations to exist, the determinant of $(\underline{V} - E_\alpha \underline{1})$
 $\det(\underline{V} - E_\alpha \underline{1}) = |\underline{V} - E_\alpha \underline{1}| = 0$. $E_\alpha = \lambda$ for convenience

If you don't know this don't worry. But you should look it up - any P. chemist etc. needs to know some linear algebra; in particular diagonalizing a matrix.

For a 2x2 problem, det A is

$$\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = a_{11}a_{22} - a_{12}a_{21}$$

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So ,

$$\begin{vmatrix} a_{11} - \lambda & a_{12} \\ a_{21} & a_{22} - \lambda \end{vmatrix} = 0 \quad \begin{aligned} & (\lambda - a_{11})(\lambda - a_{22}) - a_{12}a_{21} \\ & = \lambda^2 - (a_{11} + a_{22})\lambda + a_{11}a_{22} - a_{12}a_{21} = 0 \end{aligned}$$

$$\lambda_{1,2} = \frac{a_{11} + a_{22}}{2} \pm \frac{1}{2} \sqrt{(a_{11} + a_{22})^2 - 4(a_{11}a_{22} - a_{12}a_{21})} \quad \text{eigenvalues}$$

And the eigenvectors are obtained by using the eigenvalues one at a time in the linear equations.

$$C_{\alpha}^i \quad \alpha=1 \Rightarrow \lambda_1$$

$$C_{\alpha}^i \quad \alpha=2 \Rightarrow \lambda_2$$

$$(a_{11} - \lambda_1) c_1^1 + (a_{12}) c_1^2 = 0$$

$$a_{21} c_1^1 + (a_{22} - \lambda_1) c_1^2 = 0$$

2 eqs in 2 unknowns,

can solve.

$$(a_{11} - \lambda_2) c_2^1 + a_{12} c_2^2 = 0$$

$$a_{21} c_2^1 + (a_{22} - \lambda_2) c_2^2 = 0$$

2 eqs in 2 unknowns.

Lets apply to problem at hand:

$$a_{11} = a_{22} = 0 \quad a_{12} = a_{21} = e\epsilon \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta \int_0^{\infty} dr r^2$$

$$\otimes \psi_{200}(r\theta\varphi) \underbrace{r \cos\theta}_z \psi_{210}(r\theta\varphi)$$

From $\psi_{nlm}(r\theta\varphi) = Y_{lm}(\theta, \varphi) R_n(r)$ that we worked out you show that

$$a_{12} = a_{21} = -3a_0 e\epsilon \quad a_0 = \hbar^2 / 2me^2$$

$$\lambda_{1,2} = + \frac{0}{2} \pm \frac{1}{2} \sqrt{0^2 - 4(0 - (-3a_0 e\epsilon))^2} = \mp 3a_0 e\epsilon$$

The eigenvectors from : N.B. λ_1 is the $-3a_0 e\epsilon$ eigenvalue

$$+3a_0 e\epsilon c_1^1 - 3a_0 e\epsilon c_1^2 = 0 \Rightarrow c_1^1 = c_1^2$$

$$-3a_0 e\epsilon c_1^1 + 3a_0 e\epsilon c_1^2 = 0$$

$$-3a_0 e\epsilon c_2^1 - 3a_0 e\epsilon c_2^2 = 0 \Rightarrow c_2^1 = -c_2^2$$

$$3a_0 e\epsilon c_2^1 + 3a_0 e\epsilon c_2^2 = 0$$

Since these eigenvectors are orthonormal,

$$c_1^1 = c_1^2 = \frac{1}{\sqrt{2}} \quad c_1 = \left(\frac{1}{\sqrt{2}} \quad \frac{1}{\sqrt{2}} \right)^T \quad c_2 = \left(\frac{1}{\sqrt{2}} \quad -\frac{1}{\sqrt{2}} \right)^T$$

$$\sum_{i=1}^2 c_1^i c_1^i = \frac{1}{\sqrt{2}} \frac{1}{\sqrt{2}} + \frac{1}{\sqrt{2}} \frac{1}{\sqrt{2}} = \frac{1}{2} + \frac{1}{2} = 1 \quad \sum_{i=1}^2 c_2^i c_2^i = \frac{1}{\sqrt{2}} \frac{1}{\sqrt{2}} + \left(-\frac{1}{\sqrt{2}} \right) \left(-\frac{1}{\sqrt{2}} \right) = 1$$

$$\sum_{i=1}^2 c_1^i c_2^i = \sum_{i=1}^2 c_2^i c_1^i = \left(\frac{1}{\sqrt{2}} \frac{1}{\sqrt{2}} + \frac{1}{\sqrt{2}} \left(-\frac{1}{\sqrt{2}} \right) \right) = \frac{1}{2} - \frac{1}{2} = 0.$$

These are orthonormal as advertised.

So the state $\frac{1}{\sqrt{2}} (|2S_0\rangle + |2P_0\rangle)$ has energy (shift) $-3ea_0 \epsilon$
 $\frac{1}{\sqrt{2}} (|2S_0\rangle - |2P_0\rangle)$ " $+3ea_0 \epsilon$

$$f(\underline{R} + \underline{r}_1) = f(R) + \sum_{\alpha} \underline{r}_{1\alpha} \frac{df(R)}{dR_{\alpha}} \Big|_R + \frac{1}{2} \sum_{\alpha} \sum_{\beta} r_{1\alpha} r_{1\beta} \frac{d^2 f}{dR_{\alpha} dR_{\beta}}$$

~~$$\frac{1}{|\underline{R} + \underline{r}_1|} = \frac{1}{R}$$~~

$$f(R) = \frac{1}{R}$$

$$\frac{df}{dR_{\alpha}} = \frac{d}{dR_{\alpha}} \frac{1}{R} = \frac{d}{dR_{\alpha}} \frac{1}{\left(\sum_{\mu} R_{\mu}^2\right)^{1/2}} = -\frac{1}{2} \frac{\frac{d}{dR_{\alpha}} \sum_{\mu} R_{\mu}^2}{\left(\sum_{\mu} R_{\mu}^2\right)^{3/2}} = -\frac{\sum_{\mu} \delta_{\alpha\mu} R_{\mu}}{R^3}$$

$$\frac{d^2 f}{dR_{\alpha} dR_{\beta}} = -\frac{d}{dR_{\beta}} \frac{R_{\alpha}}{\left(\sum_{\mu} R_{\mu}^2\right)^{3/2}} = -\left[\frac{\delta_{\alpha\beta}}{\left(\sum_{\mu} R_{\mu}^2\right)^{3/2}} - \frac{3}{2} \frac{2R_{\alpha} R_{\beta}}{\left(\sum_{\mu} R_{\mu}^2\right)^{5/2}} \right] = -\left[\frac{\delta_{\alpha\beta}}{R^3} - \frac{3R_{\alpha} R_{\beta}}{R^5} \right]$$

$$\frac{1}{|\underline{R} + \underline{r}_2 - \underline{r}_1|} = \frac{1}{R} + (\underline{r}_2 - \underline{r}_1) \cdot \nabla_{\underline{r}_2 - \underline{r}_1} \left(\frac{1}{|\underline{R} + \underline{r}_2 - \underline{r}_1|} \right) \Big|_{\underline{R} + \underline{r}_2} = \frac{1}{R} + r_2 \cdot \nabla_{r_2} \frac{1}{|\underline{R} + \underline{r}_2|}$$

$$o\left(\frac{1}{R}\right) \quad \frac{1}{R} + \frac{1}{R} - \frac{1}{R} - \frac{1}{R}$$

$$o\left(\frac{1}{R^3}\right) \quad + (\underline{r}_2 - \underline{r}_1) \cdot \nabla_{(\underline{R} + \underline{r}_2 - \underline{r}_1)} \frac{1}{|\underline{R} + \underline{r}_2 - \underline{r}_1|} - r_2 \cdot \nabla_{\underline{R} + \underline{r}_2} \frac{1}{|\underline{R} + \underline{r}_2|} - (-\underline{r}_1) \cdot \nabla_{\underline{R} - \underline{r}_1} \frac{1}{|\underline{R} - \underline{r}_1|}$$

~~$$o\left(\frac{1}{R^3}\right) = (\underline{r}_2 - \underline{r}_1) \cdot \nabla \frac{1}{R} - r_2 \cdot \nabla \frac{1}{R} + r_1 \cdot \nabla \frac{1}{R} = 0$$~~

$$o\left(\frac{1}{R^5}\right) \quad [(\underline{r}_2 - \underline{r}_1)(\underline{r}_2 - \underline{r}_1) - r_2 r_2 - (-\underline{r}_1)(-\underline{r}_1)] : \frac{1}{2} \nabla_R \nabla_R$$

$$= (r_2 r_2 + r_1 r_1 - 2r_1 r_2 - r_2 r_2 - r_1 r_1 = -2r_1 r_2) : \frac{1}{2} \nabla_R \nabla_R = -\underline{r}_1 \underline{r}_2 : \frac{\nabla \nabla}{R^5}$$

Therefore $V = -e^2 (\underline{r}_1 \cdot \nabla_R) (\underline{r}_2 \cdot \nabla_R) \frac{1}{R} = -e^2 \sum_{\alpha} \sum_{\beta} r_{1\alpha} r_{2\beta} \nabla_{R_{\alpha}} \nabla_{R_{\beta}} \frac{1}{R}$

$$= +e^2 \left[\frac{\sum_{\alpha} \sum_{\beta} r_{1\alpha} r_{2\beta} \delta_{\alpha\beta}}{R^3} - \frac{3 \sum_{\alpha} \sum_{\beta} r_{1\alpha} r_{2\beta} R_{\alpha} R_{\beta}}{R^5} \right] = +e^2 \left[\frac{\underline{r}_1 \cdot \underline{r}_2}{R^3} - \frac{3(\underline{r}_1 \cdot \underline{R})(\underline{r}_2 \cdot \underline{R})}{R^5} \right]$$

Anharmonic Oscillator

$$H = \frac{1}{2}(p^2 + x^2) + \epsilon x^4$$

$$E_n = (n + \frac{1}{2})$$

$\langle n' | x^4 | n \rangle$ are zero unless $(n' - n) = 0, \pm 2, \pm 4$.

$$\langle n-4 | x^4 | n \rangle = f_1(n)$$

$$\langle n-2 | x^4 | n \rangle =$$

$$\langle n | x^4 | n \rangle$$

$$\langle n+2 | x^4 | n \rangle$$

$$\langle n+4 | x^4 | n \rangle$$

$$E_n = (n + \frac{1}{2}) + \frac{3}{2} \epsilon (n^2 + n + \frac{1}{2}) - \frac{\epsilon^2}{8} (34n^3 + 57n^2 + 55n + 21)$$

$$(E_{n+1} - E_n) = \omega_{n+1,n} = 1 + 3\epsilon(n+1) - \frac{\epsilon^2}{4} (\text{pos}), > 0$$

Careful, can't use this when n "very large", otherwise correction breaks down.

(see Powell & Crossman p 387)

This means no longer single line of ω_0 in
HO spectrum

$$E_1 - E_0 = \frac{1}{2} \quad E_2 - E_1 = \frac{1}{2} \text{ in}$$

For large n get classical