Time Independent Perturbation Theory Contd.

Keep in mind that if you can come up with arguments that make the matrix element is zero, it will make the calculation easier as we had in the HO example.

If for some obsevable Ω we have $[\Omega, H_0] = [\Omega, H_p] = 0$ we can find simultaneous eigenstates for H_0 and H_p such that

$$|\phi_n\rangle = |n, \omega_i\rangle$$

$$0 = \langle n', \omega_j|[\Omega, H_p]|n, \omega_i\rangle$$

$$0 = \omega_j \langle n'\omega_j|H_p|n, \omega_i\rangle - \omega_i \langle n'\omega_j|H_p|n, \omega_i\rangle$$

which implies that the matrix elements are zero if $\omega_j \neq \omega_i$

EX1: Let $H_p = x^2$. Parity commutes with x^2 and with the Hamiltonian of the HO. We conclude that x^2 can't have any non-zero matrix elements between two HO eigenstates $|\phi_n\rangle, |\phi_m\rangle$ unless the difference $n - m$ is even number (same parity).

EX2: Let $H_p = x$. In this case, it doesn't commute with the parity operator and in fact changes sign under parity. This means that $\langle \phi_m|H_p|\phi_n\rangle$ can be non-zero only if $|\phi_n\rangle$ and $|\phi_m\rangle$ have different parity, i.e. if the difference $m - n$ is odd.

EX3: Assume H_0 is rotationally symmetric, so its eigenstates can be chosen as eigenstates to L^2 and L_z: $|\alpha, \ell, m\rangle$. Now if $H_p \propto T_k^q$ (some tensor operator of rank k) then we know that

$$\langle \alpha', \ell', m'|H_p|\alpha, \ell, m\rangle = 0$$

unless $m' = q + m$ and $|\ell - k| \leq \ell' \leq |\ell + k|$. This can be used to reduce the number of matrix elements one has to calculate.

0.1 Example 2: The Stark Effect

The unperturbed hamiltonian of the hydrogen atom is given by $H_0 = \frac{p^2}{2m} - \frac{e^2}{r}$. the eigenfunctions are $|n, \ell, m\rangle$ and the energies are $E_{n\ell m} = E_n = -R_y \frac{1}{n^2}$. Introducing the perturbation by putting the Hydrogen atom in an electric field that is much smaller than the field of the nucleus. Let the electric field be homogeneous and in the z-direction, $\vec{\epsilon} = \epsilon \hat{z}$ (assume the atom is between the two plates of a capacitor). The potential energy due to the perturbation is $H_p = e\epsilon z$. Now, what is $|\psi'_{100}\rangle$? and E'_{100}? The first order correction to the energy is given by:

$$E'_{100} = E_{100} + \langle 100|e\epsilon z|100\rangle$$

z has odd parity and the wave function is even under parity so

$$\langle 100|e\epsilon z|100\rangle = 0$$

There is no change in the energy of the H atom to the first order approximation. There is no dipole moment to the first order approximation because the ground state is spherically symmetric, so $E_{dip} = -\vec{P}\cdot\vec{\epsilon} = 0$.

The spherical tensor corresponding to z is T_1^0. To figure out the first order change in the wave function we have to evaluate matrix elements like

$$\langle n'\ell'm'|e\epsilon z|100\rangle$$

m' has to be zero and since $\langle n'\ell'0|z|nl0\rangle \neq 0$ only if $\ell' = \ell \pm 1$, so $\ell' = 1$ and

$$|\delta\psi_\perp\rangle = \sum_{n'>1} \frac{\langle n'10|e\epsilon z|100\rangle}{-R_y(1-\frac{1}{n^2})}|n'10\rangle$$

which is our modified state. The denomenator is negative indicating that the expectation value for the position of the electron is negative, which means the electron has a larger probability to be below $z = 0$.

Second order:

$$E'_{100} = -R_y - \sum_{n'=2}^{\infty} \frac{|\langle n'10|e\epsilon z|100\rangle|^2}{R_y(1-\frac{1}{n^2})}$$

Putting the H atom in the electric field reduces its energy because the electric field induces a dipole moment.

$$E'_{100} = -R_y - \epsilon^2(\sum_{n'=2}^{\infty} \frac{|\langle n'10|ez|100\rangle|^2}{R_y(1-\frac{1}{n^2})})$$

The term in () is proportional to the polarizability. As a result, a hydrogen atom is attracted towards a region of larger electrical fields (insulators are attracted to charged objects).

Degenerate Case

So far we have always assumed that all eigenvalues of the Hamiltonian H_0 are non-degenerate.

If $E_n = E_m$ the Hamiltonian is degenerate. An example is the Hydrogen Atom that can be described with eigenstates

$$|nlm>, \text{the energy depends only on } n, \text{ i.e } E_n = -Ry\frac{1}{n^2}$$

and only its ground state is non-degenerate.

For the degenerate states, we need to make sure that the overlap integral $< m|H_p|n >$ is zero whenever $E_n = E_m$. Otherwise the first-order correction to the wave function and the second order correction to the energy "blow up" (zero denominators). Formally, our derivation assumed that for each eigenstate of H_0 there is a corresponding eigenstate of $H = H_0 + H_P$ that smoothly converges to the original one as H_P goes to zero. However, for degenerate eigenvalue of H_0 there are infinitely many possible eigenstates to choose from (any linear combination of eigenstates is also an eigenstate). So we have to find a specific set of eigenstates that diagonalize H_P - only those eigenstates will connect "smoothly" to the new eigenstates of $H_0 + H_P$.

To do that, we take the Hilbert space and split it into sub-spaces, each spanned by a complete set of eigenstates to H_o with the same degenerate energy E_n:

$$\mathbf{V} = \mathbf{V}_{E_1} \oplus \mathbf{V}_{E_2} \oplus \mathbf{V}_{E_3} \ldots \text{ basis set for the Hilbert space with}$$

$$\mathbf{V}_{E_1} = |1, \alpha >; \mathbf{V}_{E_2} = |2, \alpha > \ldots$$

So that for the Hydrogen atom we can now write the basis for $\mathbf{V}_{E_1}$: $|100 >$, the basis for $\mathbf{V}_{E_2}$: $|200 >, |211 >, |210 >, |21-1 >$, and similarly for the additional subspaces (higher energies). Each of the subspaces is a finite dimensional subspace, and any operator can be written as an $n \times n$ matrix if restricted within a finite dimension.

Given H_p, the expression

$$< E_2, \alpha'|H_p|E_2, \alpha >$$

gives all elements of the $n \times n$ matrix for H_p in that subspace. For each subspace for a degenerate eigenvalue of H_0 we diagonalize this matrix representing H_p.

A transformation can always be made from the old basis set to the new basis set following the steps:

- find the matrix elements of each subspace

- linearly combine the previous basis vectors to have H_p diagonal (unitary transformation yielding a new orthonormal basis of the subspace that diagonalizes both H_0 and H_p.)

Example:

We have a perturbation due to an electric field: $H_p = e\mathcal{E}z$.

- For the ground state $|100>$ (no degeneracy, no first-order change in energy)

$$|\delta\Psi_\perp>^{\text{1st order}} = e\mathcal{E}\sum_{n>1}\frac{<n10|z|100>}{-Ry(1-\frac{1}{n^2})}|n10>$$

$$\Delta E_1 = \underbrace{\Delta E_1^{\text{1st order}}}_{\to 0} + e^2\mathcal{E}^2\sum_{n>1}\frac{|<n10|z|100>|^2}{-Ry(1-\frac{1}{n^2})}$$

- For the state $|200>$
  We have 4 orthogonal sub states so we have to check the matrix elements of H_p and see if we can diagonalize.

  The selection rules for the process are that
  1- z can only couple states with $m = m'$ and
  2- the element matrix must have odd parity. Since z has odd parity if it's taken between states with the same parity we get a zero.

  The elements to calculate are thus $<210|z|200> = -3a_o$

	$|200>$	$|210>$	$|211>$	$|21-1>$
$<200|$	0	$-3a_oe\mathcal{E}$	0	0
$<210|$	$-3a_oe\mathcal{E}$	0	0	0
$<211|$	0	0	0	0
$<21-1|$	0	0	0	0

From the table values, H_p is not diagonal, so we have to combine the elements in such a way as to make it so.

Eigenvalues of the 2×2 matrix : $\mp 3a_oe\mathcal{E}$
Eigenstates, with corresponding eigenvectors: $\frac{1}{\sqrt{2}}(|200> \pm |210>)$

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Rewriting the unperturbed state:

$$|a> = \frac{1}{\sqrt{2}}(|200> + |210>)$$

$$|b> = \frac{1}{\sqrt{2}}(|200> - |210>)$$

with similar combinations for the other states, H_p in the new states is now diagonalized

$$H_p = \begin{pmatrix} -3a_o e\mathcal{E} & 0 & 0 & 0 \\ 0 & +3a_o e\mathcal{E} & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

and we can evaluate the equation

$$\Delta E_2^{\text{1st order}} = <a|H_p|a> = -3a_o e\mathcal{E}$$
$$\Delta E_2^{\text{1st order}} = <b|H_p|b> = +3a_o e\mathcal{E}$$

There is no dipole moment in the ground state for the 1st order perturbation.

To the 2nd order, there is an induced dipole moment which interacts linearly with the electric field and causes the 2nd order perturbation. However, the 1st excited state ($n = 2$) apparently *does* have a non-zero "permanent" dipole moment, so the energy changes in first order. More specifically:

- combining 2 states creates a dipole moment

- if there's no electric field, the Hydrogen atom wave function can be chosen arbitrarily within each subspace. It is always possible to choose symmetric (standard) wave functions.

- For even the slightest electric field, degeneracy causes a "spontaneous breaking" of rotational symmetry selecting new combination of states with non-zero intrinsic dipole moments (since it "costs no energy").These intrinsic dipoles interact with the field to give a a first-order change in the energy.