Van der Walls Probblem Set up

Scale of electron chatrge ~ a_0
Distance between the two charges $= R\hat{n}$, we have $R >> a_0$
$H_0 = H_A + H_B$ is the none perterbed Hamiltonian
$H = H_0 + W$ where W is the perterbation term, which is the dipole-dipole interaction.

let $\vec{r}_a$ represents the vector pointing from proton A to electron A
let $\vec{r}_b$ represetns the vector pointing from proton B to electron B

From classical E&M
$\vec{\mu}_A = e\vec{r}_a$
$\vec{\mu}_b = e\vec{r}_b$
$W = \frac{\vec{\mu}_A \cdot \vec{\mu}_b - 3(\vec{\mu}_A \cdot \hat{n})(\vec{\mu}_B \cdot \hat{n})}{R^3}$

let
$\hat{n} = \hat{z} \rightarrow \frac{e^2}{R^3}(x_a x_b + y_a y_b - 2z_a z_b)$
and the unperterbed eigenstate $|\psi^A_{nlm}\rangle \, |\psi^B_{n'l'm'}\rangle$
and Energy perterbation $E = E^0_n + E^0_{n'}$

1st order term is zero : why? (symmetrical in $\hat{R}$, odd R ?)
2nd order term $\rightarrow -\frac{C}{R^6}$, find dimension for C

Degenerate Perterbation Theory

Earlier formula $|n\rangle = \sum_{m \neq n} \frac{\langle m_0|H_1|n_0\rangle}{E^0_n - E^0_m} |m_0\rangle + ...$
Note that his **cannot** be used when $E^0_n = E^0_m$
Now suppose our Hamiltonian have degenerate eigenenergy
Let $H_0 |n_0, r\rangle = E^0_n |n_0, r\rangle$ where r label the degenerate states and $r \in \{1, 2, ..., D\}$

Thoght process: We stratigically choose a particuliar linear combination of $|n_0, r\rangle$ such that the matrix elements corresponding to problematic demoninator also vanish.

We will show next that this is accomplished by:
choose $|\psi^0_{n,r}\rangle = \sum_s c_{r,s} |n_0, s\rangle$ s.t. $\langle\psi^0_{n,r}| \, H_1 \, |\psi^0_{n,r'}\rangle = E'_n \delta_{r,r'}$

Proof:

let $\left|\psi^0_{n,r}\right\rangle = \sum_s c_{r,s} \left|n_0, s\right\rangle$
$\left\langle\psi_{r,s}\right| \left|\psi_{r',s}\right\rangle = \delta_{r,r'}$
LHS = $\sum_{s,s'} c^*_{r,s} c_{r',s'} \left\langle n_0, s \middle| n_0, s'\right\rangle = \sum_s c^*_{r,s} c_{r',s} = \delta_{r,r'}$ (1)
Need to solve
$(H_0 + \lambda H_1)(\left|\psi^0_{n,r}\right\rangle + \lambda \left|\psi^1_{n,r}\right\rangle) = (E^0_n + \lambda E^1_n)(...)$

0th ordr in λ : $H_0 \left|\psi^0_{n,r}\right\rangle = E_0 \left|\psi^0_{n,r}\right\rangle$
1st order in λ: $H_0 \left|\psi^1_{n,r}\right\rangle + H_1 \left|\psi^0_{n,r}\right\rangle = E^0_n \left|\psi^1_{n,r}\right\rangle + E^1_n \left|\psi^0_{n,r}\right\rangle$
1st term of LHS = $\left\langle\psi^0_{n,s} H_0 \middle| \psi^1_{n,r}\right\rangle = E^0_n \left\langle\psi^0_{ns} \middle| \psi^1_{n,r}\right\rangle = E^0_n \delta_{s,r}$
2nd term of LHS = $\left\langle\psi^0_{n,s} H_1 \left|\psi^1_{n,r}\right\rangle\right\rangle = E^1_n \left\langle\psi^0_{ns} \middle| \psi^1_{n,r}\right\rangle\rangle = E^1_n \delta_{s,r}$, which is just (1)

Example: Stark-effect of the n=2 state of H atom

$H = H_0 + H_1$, $H_1 = eEr\cos\theta$
Unperterbed eigenstates: $\left|2,0,0\right\rangle$, $\left|2,1,0\right\rangle$, $\left|2,1,1\right\rangle$, $\left|2,1,-1\right\rangle$
with $E_2 = -\frac{1}{4}(\frac{me^4}{2\hbar^2})$, which means energy is degenerate

will see that

$$H_1 = \begin{pmatrix} 0 & \Delta & 0 & 0 \\ \Delta & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

Note that:

1. $\left\langle nlm\right| H_1 \left|n', l', m'\right\rangle \neq 0$ only for $m = m'$
   This is because for ϕ term for the inneerprocut, we have the intergral $\int_0^{2\pi} e^{-i(m-m')\phi} = 2\pi\delta_{m,m'}$
2. $\left\langle n, l, m\right| H_1 \left|n', l', m'\right\rangle \neq 0$ only for $l' = l \pm 1$