Lecture #19 Nov 3.

DC Electric fields: Stark effect:

The dipole approximation to the electric field ~~operator~~ part of the Hamiltonian is

$$H_E = -\vec{d}\cdot\vec{E}(R)$$

Looks similar to $H_B = -\vec{\mu}\cdot\vec{B}$, but what is different?

- no permanent dipole moment in the ground state (violates time-reversal symmetry)
- $\vec{d}$ has odd parity $\Rightarrow$ cannot shift a level of definite parity to first order

$\langle\psi|\vec{d}|\psi\rangle = 0$ if $|\psi\rangle$ has definite parity (e.g. eigenstate of H_A)

Shifts must occur in second order:

$$E_E = +\sum_{|\psi'\rangle} \frac{\langle\psi|\vec{d}\cdot\vec{E}|\psi'\rangle\langle\psi'|\vec{d}\cdot\vec{E}|\psi\rangle}{E_\psi - E_{\psi'}}$$

looks alot like the light shift!

$$E_E = \vec{E}\cdot \underbrace{\sum_{|\psi'\rangle} \frac{\langle\psi|\vec{d}|\psi'\rangle\langle\psi'|\vec{d}|\psi\rangle}{E_\psi - E_{\psi'}}}_{\text{has possible scalar, vector, \& 2nd rank tensor.}} \cdot\vec{E}$$

For DC fields, $\vec{E}^* = \vec{E}$, so $(\vec{E} \times \vec{E}^*) = 0$.

No vector part of DC stark shift.

in addition, the tensor part will involve only the $q=0$ term, because the initial and final states are the same. (m_F is unchanged)

The scalar + tensor polarizabilities are in general hard to calculate, because they involve sums over electronic matrix elements, including states in the continuum!

Usually people use experimental values:

$$H_E = -\frac{1}{2}\alpha_0 E_z^2 \underbrace{- \overbrace{\frac{1}{2}\alpha_2 E_z^2 \frac{3J_z^2 - J(J+1)}{J(2J-1)}}^{\text{essentially the } T^2_{q=0} \text{ part of } \vec{d}\vec{d}}}_{\text{only for } J > 1/2}$$

This ignores Hyperfine energies + I. The addition of another vector angular momentum $\vec{I}$ gives,

$$H_E = -\frac{1}{2}\alpha_0 E_z^2 - \frac{1}{2}\alpha_2 E_z^2 \frac{\left(3m_F^2 - F(F+1)\right)\left(3X(X-1) - 4F(F+1)J(J+1)\right)}{(2F+3)(2F+2)(2F-1)F(2J-1)J}$$

where $X = F(F+1) + J(J+1) - I(I+1)$

Note: the $T^2_{q=0}$ part of a 2^{nd} rank tensor always looks like $\left(F_z^2 - \frac{F^2}{3}\right)$

In general α_0, α_v are very small, unless two opposite parity energy levels are near each other. (e.g. Hydrogen 2s, 2p are pretty close)

e.g. α_0 for ^{87}Rb ground state is

$$\alpha_0 \cong 0.080 \ Hz/(V/cm)^2$$

For 1 gauss field, the Zeeman shift $\simeq$ 1 MHz (700 kHz)

an equivalent ~~shift~~ Stark shift would require ~ 3.5 kV/cm!

Adding a B-field simultaneous to an E field gets complicated unless $\vec{B} \parallel \hat{E}$.

Stark effect: linear vs. quadratic shifts.

Due to parity symmetry and time-reversal symmetry, we know that in the absence of any fields, there is no permanent electric dipole.

Another way to say this is that since $\vec{d}$ is an odd operator, its expectation-value with any state of good parity (+1 or -1) is zero.

$\hat{d}$ only connects states of different parity.

This implies that since $\langle\Psi|\hat{d}|\Psi\rangle = 0$, the lowest order energy shift scales as $|\vec{E}|^2$. So why do polar molecules seem to have a linear dipole shift?

Example Hydrogen 2p + 2s states
The 2s + $2p_{1/2}$ states are split by ~1GHz
(ie they are nearly degenerate) $E_{2s} > E_{2p\,1/2}$
($\Delta_{2s\leftrightarrow 2p_{3/2}} \simeq 11\,GHz$)

Look at the coupling to each state

$\langle 2s|d\cdot E|2s\rangle = 0$

$\langle 2p_{1/2}|d\cdot E|2p_{1/2}\rangle = 0$

$$\langle 2s|d\cdot E|2p_{1/2}\rangle = eE\langle 2s|z|2p_{1/2}\rangle = eE\underbrace{\langle 2s|z|210\rangle}_{\sim a_0/2}\underbrace{\langle 210|2p_{1/2}\rangle}_{-1/\sqrt{3}}$$

approximate order

$$\sim \frac{eEa_0}{2\sqrt{3}} \equiv \gamma E$$

$$H = \begin{pmatrix} \frac{\Delta_{lamb}}{2} & -\gamma E \\ -\gamma E & \frac{\Delta_{lamb}}{2} \end{pmatrix}$$

diagonalize

$$E_{Stark} = \pm\sqrt{\left(\frac{\Delta_{lamb}}{2}\right)^2 + (\gamma E)^2}$$

at low fields, $E_{Stark} \cong -\frac{\Delta_{lamb}}{2} - \frac{\gamma^2 E^2}{\Delta_{lamb}}$ } 2nd order perturbation result

at high fields

$E_{Stark} \simeq \gamma E \rightarrow$ linear.

in systems where the splitting between opposite parity states is really small, it will always look like it has a linear stark shift. (e.g. the Famous ammonia ~~atom~~ molecule.)

See links on Femto-second frequency Combs provided on the Course web page