Schrödinger eqn calc of χ.

$\hat{H}_0$ is hamiltonian for atom

$\hat{V}(t) = -\hat{\vec{\mu}} \cdot \vec{E}(t)$ is perturbing interaction

$\hat{\vec{\mu}} = -e\hat{\vec{r}}$ dipole operator

$\vec{E}(t) = \sum_p \vec{E}(\omega_p) e^{-i\omega_p t}$ p is +/-

unperturbed eigenstates of atom:

$$\Psi_n(\vec{r},t) = u_n(\vec{r}) e^{-i\omega_n t}$$

w/ orthonormality:

$$\int u_m^* u_n \, d^3r = \delta_{mn}$$

so that

$$\hat{H}_0 u_n = E_n u_n$$

Time-dependent perturbation theory.

full Hamiltonian is

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}(t) \qquad 0 < \lambda < 1$$

if $\Psi(\vec{r},t)$ is a solution to the full $\hat{H}$: $\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}$

We can express this solution as an expansion:

$$\Psi(\vec{r},t) = \Psi^{(0)}(\vec{r},t) + \lambda \Psi^{(1)}(\ ) + \lambda^2 \Psi^{(2)}(\ ) + \cdots$$

collect terms of equal order in λ

0^{th} order: $i\hbar \frac{\partial \Psi^{(0)}}{\partial t} = \hat{H}_0 \Psi^{(0)}$ unperturbed case

1^{st} order: $i\hbar \frac{\partial \Psi^{(1)}}{\partial t} = \hat{H}_0 \Psi^{(1)} + \hat{V} \Psi^{(0)}$

N^{th} order: $i\hbar \frac{\partial \Psi^{(N)}}{\partial t} = \hat{H}_0 \Psi^{(N)} + \hat{V} \Psi^{(N-1)}$

we'll assume the electron is initially in the ground state.

$$\Psi(\vec{r}, t=0) = u_g(\vec{r}) \qquad \Psi^{(0)}(\vec{r},t) = u_g(\vec{r}) e^{-iE_g t/\hbar}$$

Now we assume that unpert. solutions forms a complete set.
we can represent any order N in that basis

$$\Psi^{(N)}(\vec{r},t) = \sum_{l} a_l^{(N)}(t)\, u_l(\vec{r})\, e^{-i\omega_l t} \qquad \omega_l = E_l/\hbar$$

in first-order PT we're looking for $\Psi^{(1)}$

general case

$$\rightarrow\ i\hbar \sum_l \dot{a}_l^{(N)} u_l(\vec{r}) e^{-i\omega_l t} = \sum_l a_l^{(N-1)} \hat{V} u_l(\vec{r}) e^{-i\omega_l t}$$

1st order: if there is only the ground state at $t=0$,

$$i\hbar \sum_l \dot{a}_l^{(1)} u_l(\ ) e^{-i\omega_l t} = \hat{V} u_g(\ ) e^{-i\omega_g t}$$

We want to extract an eqn. for the coeffic:
mult by $u_m^*(\ )$ and integrate. Use orthogonality

$$\rightarrow\ i\hbar \sum_l \dot{a}_l^{(N)} \int u_m^* u_l e^{-i\omega_l t} d^3r = i\hbar\, \dot{a}_m^{(N)} e^{-i\omega_m t}$$

$$= \sum_l a_l^{(N-1)} \int u_m^* \hat{V} u_l e^{-i\omega_l t} d^3r \equiv \sum_l a_l^{(N-1)} V_{ml} e^{-i\omega_m t}$$

Finally, we have set of eqns:

$$\dot{a}_m^{(N)} = \frac{1}{i\hbar} \sum_l a_l^{(N-1)} V_{ml} e^{i\omega_{ml} t} \qquad \omega_{ml} = \omega_m - \omega_l$$

This is actually a matrix equation: Suppose 3 levels

$$\begin{pmatrix} \dot{a}_1^{(1)} \\ \dot{a}_2^{(1)} \\ \dot{a}_3^{(1)} \end{pmatrix} = \frac{1}{i\hbar} \begin{pmatrix} V_{11} & V_{12} & V_{13} \\ V_{21} & V_{22} & V_{23} \\ V_{31} & V_{32} e^{i\omega_{32} t} & V_{33} \end{pmatrix} \begin{pmatrix} a_1^{(0)} \\ a_2^{(0)} \\ a_3^{(0)} \end{pmatrix}$$

insert $e^{i\omega_{ml} t}$ terms on off diagonals.

we can evaluate $a_m^{(N)}(t)$ by integrating:

$$a_m^{(N)}(t) = \frac{1}{i\hbar} \sum_l \int_{-\infty}^{t} dt'\, V_{ml}(t')\, a_l^{(N-1)}(t')\, e^{i\omega_{ml} t'}$$

Solutions:

1) system initially in ground state

2) $V_{m\ell}(t') = -\sum_p \vec{\mu}_{m\ell} \cdot \vec{E}(\omega_p) e^{-i\omega_p t'}$

$$\vec{\mu}_{m\ell} = \int u_m^* \hat{\mu} u_\ell \, d^3r \quad = \text{electric dipole transition moment.}$$

3) calc. 1st order term → linear response, $\chi^{(1)}$

$$a_m^{(1)}(t) = \frac{1}{\hbar} \sum_p \frac{\vec{\mu}_{mg} \cdot \vec{E}(\omega_p)}{\omega_{mg} - \omega_p} e^{i(\omega_{mg} - \omega_p)t}$$

4) calc. 2nd order term: involves a second sum over input fields
→ $\chi^{(2)}$

$$a_n^{(2)}(t) = \frac{1}{\hbar^2} \sum_{pq} \sum_m \frac{(\vec{\mu}_{nm} \cdot \vec{E}(\omega_q))(\vec{\mu}_{mg} \cdot \vec{E}(\omega_p))}{(\omega_{ng} - \omega_p - \omega_q)(\omega_{mg} - \omega_p)} e^{i(\omega_{ng} - \omega_p - \omega_q)t}$$

add up ω's

$$V_{nm} \quad a_m \quad e^{i\omega_{nm}t'}$$
$$-\omega_q + \omega_{mg} - \omega_p + \omega_{nm} = \omega_{ng} - \omega_p - \omega_q.$$

5) 3rd order ...

Calculation of suscept.

<u>Linear</u>

recall classical calc: $\vec{P} = \chi^{(1)}\vec{E} = N_a \vec{p}$

atomic density · dipole moment.

QM: $\langle \vec{p} \rangle = \langle \Psi | \vec{\mu} | \Psi \rangle$ expectation value.

remember we are expanding Ψ in pert. series.

→ expansion of $\vec{p}$

$$\langle p^{(1)} \rangle = \langle \Psi^{(0)} | \vec{\mu} | \Psi^{(1)} \rangle + \langle \Psi^{(1)} | \vec{\mu} | \Psi^{(0)} \rangle$$

$$|\Psi^{(1)}\rangle = \sum_m a_m^{(1)}(t) |u_\ell\rangle e^{-i\omega_m t}$$

$$\langle p^{(1)}\rangle = \frac{1}{\hbar}\sum_p\sum_m\left(\frac{\vec{\mu}_{gm}\left(\vec{\mu}_{mg}\cdot\vec{E}(\omega_p)\right)}{\omega_{mg}-\omega_p}e^{-i\omega_p t} + \frac{\left(\vec{\mu}_{mg}\cdot\vec{E}(\omega_p)\right)^*\vec{\mu}_{mg}}{\omega_{mg}^*-\omega_p}e^{+i\omega_p t}\right)$$

sum is over $\pm\,\omega_p$'s

want to separate out $e^{-i\omega_p t}$

$\therefore$ let $\omega_p \to -\omega_p$ in second term

still sum of $\pm\,\omega_p$'s

note $E(-\omega_p) = E^*(\omega_p)$

let ω_{mg} be complex to allow for damp.

$\omega_{mg} = \omega_{mg}^{\circ} - i\Gamma_m/2$

Need more inclusive theory to do right.

$$\langle p^{(1)}\rangle = \frac{1}{\hbar}\sum_p\sum_m\left(\frac{\vec{\mu}_{gm}\left(\vec{\mu}_{mg}\cdot\vec{E}(\omega_p)\right)}{\omega_{mg}-\omega_p} + \frac{\vec{\mu}_{mg}\left(\vec{\mu}_{gm}\cdot\vec{E}(\omega_p)\right)}{\omega_{mg}^*+\omega_p}\right)e^{-i\omega_p t}$$

Finally

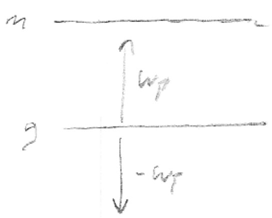
$$\vec{P}^{(1)} = N_a\langle\vec{p}^{(1)}\rangle \;\to\; \sum_p \vec{P}^{(1)}(\omega_p)\,e^{-i\omega_p t}$$

$$P_i^{(1)}(\omega_p) = \sum_j \chi_{ij}^{(1)}E_j(\omega_p) \qquad i,j \text{ cartesian indices.}$$

$$\chi_{ij}^{(1)}(\omega_p) = \frac{N_a}{\hbar}\sum_m\left(\frac{\mu_{gm}^{i}\,\mu_{mg}^{j}}{\omega_{mg}-\omega_p} + \frac{\mu_{mg}^{i}\,\mu_{gm}^{j}}{\omega_{mg}^*+\omega_p}\right)$$

note appearance of resonant denominator

$$D_R(\omega_p) = \omega_{mg}^{\circ} - \omega_p - i\Gamma_m/2$$



and anti-res.

$$D_a(\omega_p) = \omega_{mg}^{\circ} + \omega_p + i\Gamma_m/2$$

if we add both terms $\to$ denom is product of both:

$$|\omega_{mg}|^2 - \omega_p^2 - \omega_p\omega_{mg}^* + \omega_p\omega_{mg}$$

compare to classical $\omega_{mg}^{\circ} \to \omega_0$ $\qquad D(\omega) = \omega_0^2 - \omega^2 - 2i\omega\gamma$

$$\omega_0^2 - \omega_p^2 - i\omega_p\Gamma_m + \Gamma_m^2/4$$

so $\gamma = \Gamma_m/2$

and $\Gamma_m/2 \ll \omega$.

Calc. of $\chi^{(2)}$

2^{nd} order expansion of dipole moment:

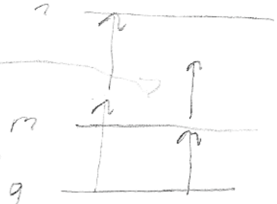
$$\langle \hat{p}^{(2)} \rangle = \langle \Psi^{(0)} | \hat{\mu} | \Psi^{(2)} \rangle + \langle \Psi^{(1)} | \hat{\mu} | \Psi^{(1)} \rangle + \langle \Psi^{(2)} | \hat{\mu} | \Psi^{(0)} \rangle$$

see result in Boyd.

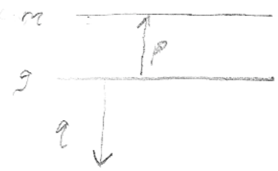
comments:

- symmetries in $\chi^{(2)}$ or $\chi^{(3)}$ are easier to connect to matrix elements
- resonant structure seen in denominators:

$$(\omega_{ng} - \omega_p - \omega_q)(\omega_{mg} - \omega_p)$$



$$(\omega_{ng}^* + \omega_q)(\omega_{mg} - \omega_p)$$



$(\omega_{ng}^* + \omega_q)(\omega_{mg}^* + \omega_p + \omega_q)$ all antiresonant.