Schrödinger eqn calc of χ

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

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

$\hat{\mu} = -e\hat{r}$ 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

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

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.

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

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

$$\psi^{(N)}(\vec{r},t) = \sum_k a_k^{(N)}(t)\, u_k(\vec{r})\, e^{-i\omega_k t} \qquad \omega_k = E_k/\hbar$$

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

general case

$$\rightarrow \; i\hbar \sum_k \dot{a}_k^{(N)} u_k(\vec{r}) e^{-i\omega_k t} = \sum_k a_k^{(N-1)} \hat{V} u_k(\vec{r}) e^{-i\omega_k t}$$

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

$$i\hbar \sum_k \dot{a}_k^{(1)} u_k(\,) e^{-i\omega_k t} = \hat{V} u_g(\,) e^{-i\omega_g t}$$

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

$$\rightarrow i\hbar \sum_k \dot{a}_k^{(N)} \int u_m^* u_k e^{-i\omega_k t}\, d^3r = i\hbar\, \dot{a}_m^{(N)} e^{-i\omega_m t}$$

$$= \sum_k a_k^{(N-1)} \int u_m^* \hat{V} u_k e^{-i\omega_k t}\, d^3r \equiv \sum_k a_k^{(N-1)} V_{mk} e^{i\omega_m t}$$

Finally, we have set of eqns:

$$\dot{a}_m^{(N)} = \frac{1}{i\hbar} \sum_k a_k^{(N-1)} V_{mk} e^{i\omega_{mk} t} \qquad \omega_{mk} = \omega_m - \omega_k$$

This is actually a matrix equation. Suppose 3 levels is

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

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

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

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

Solutions:

1) system initially in ground state

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

$$\vec{\mu}_{mg} = \int u_m^* \hat{\mu}\, u_g\, d^3r$$ = electric dipole transition moment.

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

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

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

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

add up ω's

V_{nm} a_m $e^{i\omega_{nm}t'}$

$-\omega_q + \omega_{mg} - \omega_p + \omega_{nm} = \omega_{ng} - \omega_p - \omega_q$.

5) 3rd order ...

Note direct connection btw order of TDPT and χ order, # photons

Calculation of susceptibility.

Linear

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

atomic density · dipole moment.

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

remember we are expanding ψ in pert. series.

→ expansion of $\vec{p}$

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

$$|\psi^{(1)}\rangle = \sum_m a_m^{(1)}(t) |u_g\rangle e^{-i\omega_m t}$$