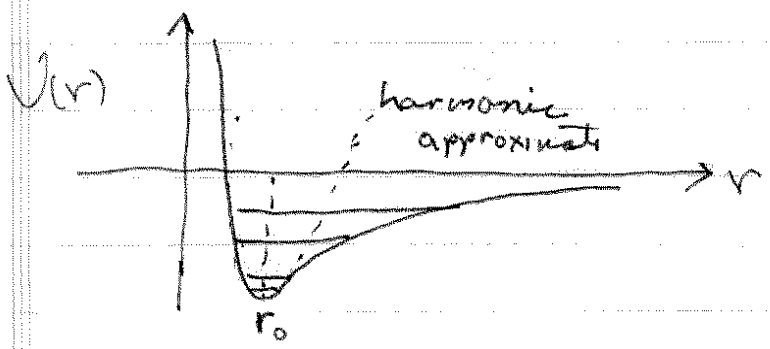
# Physics 522

## Problem Set # 7 Solutions

**Problem 1:** Ro-vibrational spectrum of $H_2$ molecule

Born-Oppenheimer potential




$$\hat{H} = \frac{\hat{p}_r^2}{2\mu} + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} + U(\hat{r})$$

Near $r_0$ the potential looks harmonic

(a) Taylor expansion about $r_0$ (equilibrium separation for $\ell = 0$)

$$r = r_0 + \delta r$$

$$U(r) = U(r_0) + (\delta r)\left.\frac{dU}{dr}\right|_{r_0} + \frac{1}{2}\left.\frac{d^2U}{dr^2}\right|_{r_0}(\delta r)^2 + \frac{1}{3!}\left.\frac{d^3U}{dr^3}\right|_{r_0}(\delta r)^3 + \frac{1}{4!}\frac{d^4U}{dr^4}(\delta r)^4 + \mathcal{O}(\delta r^5)$$

$\left.\frac{dU}{dr}\right|_{r_0}$ = 0 at minimum

$$\equiv U(r_0) + \frac{1}{2}k(\delta r)^2 + \frac{1}{3!}k'(\delta r)^3 + \frac{1}{4!}k''(\delta r)^4$$

where $k \equiv \left.\frac{d^2U}{dr^2}\right|_{r_0}$

$$k' = \left.\frac{d^3U}{dr^3}\right|_{r_0}$$

$$k'' = \left.\frac{d^4U}{dr^4}\right|_{r_0}$$

Taylor expand the "angular momentum barrier" about $r_0$

$$\frac{1}{r^2} = \frac{1}{(r_0+\delta r)^2} = \frac{\left(1+\frac{\delta r}{r_0}\right)^{-2}}{r_0^2} = \frac{1}{r_0^2} - \frac{2(\delta r)}{r_0^3} + \frac{3(\delta r)^2}{r_0^4}$$

(Having used $(1+\epsilon)^n \simeq 1 + n\epsilon + \frac{n(n-1)}{2}\epsilon^2$, $\epsilon \ll 1$)

$$\Rightarrow U_{\text{eff}}(r) = U(r_0) + \frac{\hbar^2 \ell(\ell+1)}{2\mu r_0^2} + \text{corrections}$$

$$\Rightarrow \hat{H} = \hat{H}_0 + \hat{H}_1$$

$$\hat{H}_0 = \frac{\hat{p}_r^2}{2\mu} + \frac{1}{2}k(\delta\hat{r})^2 + \frac{\hbar^2\ell(\ell+1)}{2\mu r_0^2} + U(r_0)$$

$$\hat{H}_1 = \frac{1}{3!}k'''(\delta\hat{r})^3 + \frac{1}{4!}k''''(\delta\hat{r})^4 - \frac{\hbar^2\ell(\ell+1)}{\mu r_0^3}\delta\hat{r} + \frac{3}{2}\frac{\hbar^2\ell(\ell+1)}{\mu r_0^4}(\delta\hat{r})^2$$

$$\hat{H}_0 = \hat{H}_{\text{SHO}} + \text{Constant} \quad \left(\frac{\hbar^2\ell(\ell+1)}{2\mu r_0^2} + U(r_0)\right)$$

$\Rightarrow$ Zero$^{\text{th}}$ order "vibrational levels"

$$|\phi_v^{(0)}\rangle \equiv |v\rangle \qquad v = 0, 1, 2, \ldots$$

$$E_v^{(0)} = \hbar\omega\left(v+\frac{1}{2}\right) + \frac{\hbar^2\ell(\ell+1)}{2\mu r_0^2} + U(r_0)$$

$$\omega = \sqrt{\frac{k}{\mu}} \quad \text{(oscillation frequency)}$$

(b) First make dimensionless.

Characteristic scales: $r_c \equiv \sqrt{\frac{\hbar}{\mu\omega}}$ (SHO), $p_c = \sqrt{\hbar\mu\omega}$, $E_c = \hbar\omega$

where $\omega = (k/\mu)^{1/2} \Rightarrow r_c = \sqrt{\hbar}\,(k\mu)^{-1/4}$

Dimensionless variables

$$\hat{h} = \frac{\hat{H}}{\hbar\omega}, \quad \hat{y} = \frac{\delta\hat{r}}{r_c}, \quad -i\frac{d}{dy} = \frac{\hat{p}_r}{p_c} \;(\text{position representation}) \;= \hat{P}$$

$$\Rightarrow \hat{h} = \hat{h}_0 + \hat{h}_1$$

$$h_0 = \tfrac{1}{2}(\hat{y}^2 + \hat{P}^2) + \frac{\ell(\ell+1)}{2\mu r_0^2}\frac{1}{\omega} + \frac{U(r_0)}{\omega} \quad (\text{setting } \hbar \to 1)$$

$$\Rightarrow \boxed{h_0 = \left(\hat{a}^\dagger\hat{a} + \tfrac{1}{2}\right) + \frac{\ell(\ell+1)}{2r_0^2\sqrt{\mu k}} + U(r_0)\sqrt{\frac{\mu}{k}}}$$

$$h_1 = \frac{1}{3!}k'y^3\left(\frac{r_c^3}{\omega}\right) + \frac{1}{4!}k''y^4\left(\frac{r_c^4}{\omega}\right) - \frac{\ell(\ell+1)}{\mu r_0^3}y\left(\frac{r_c}{\omega}\right) + \frac{3}{2}\frac{\ell(\ell+1)}{\mu r_0^4}y^2\left(\frac{r_c^2}{\omega}\right)$$

$$\Rightarrow \boxed{h_1 = \frac{k'}{3!(k^5\mu)^{1/4}}y^3 + \frac{k''}{4!(k^3\mu)^{1/2}}y^4 - \frac{\ell(\ell+1)}{r_0^3(\mu k)^{3/4}}y + \frac{3}{2}\frac{\ell(\ell+1)}{r_0^4(\mu k)}y^2}$$

(c) We seek first order corrections to energy levels.

First note: The vibrational eigenstates of eigenstates of parity: $\hat{\Pi}|v\rangle = (-1)^v |v\rangle$.

$\Rightarrow$ Only even functions of $y$ have a non-zero mean value in a state $|v\rangle$

$$\Rightarrow E_v^{(1)} = \hbar\omega \langle v|\hat{h}_1|v\rangle$$

$$= \hbar\omega \left[ \frac{k''}{4!(k^3\mu)^{1/2}} \langle v|\hat{y}^4|v\rangle + \frac{3}{2}\frac{l(l+1)}{r_0^4(\mu k)} \langle v|\hat{y}^2|v\rangle \right]$$

We found in class

$$\langle v|\hat{y}^4|v\rangle = \frac{1}{4}\langle v|(\hat{a}+\hat{a}^\dagger)^4|v\rangle = \frac{3}{2}\left(v^2+v+\frac{1}{2}\right)$$

The remain matrix element is a familiar one:

$$\langle v|\hat{y}^2|v\rangle = \frac{1}{2}\langle v|(\hat{a}+\hat{a}^\dagger)^2|v\rangle = \frac{1}{2}\langle v|(\hat{a}^\dagger\hat{a}+\hat{a}\hat{a}^\dagger)|v\rangle$$

$$= \frac{1}{2}(2v+1) = v+\frac{1}{2} \qquad (\hat{a}^\dagger\hat{a}+\hat{a}\hat{a}^\dagger = 2\hat{N}+1)$$

$$\therefore \boxed{E_v^{(1)} = \hbar\sqrt{\frac{k}{\mu}}\left[\frac{3k''}{8(k^3\mu)^{1/2}}\left(v^2+v+\frac{1}{2}\right) + \underbrace{\frac{3l(l+1)}{2r_0^4(\mu k)}}_{\text{ro-vibrational interaction}}\left(v+\frac{1}{2}\right)\right]}$$

Note: • From the Virial theorem we can solve for the $\hat{y}^2$ contribution exactly

• The linear term, $\hat{y}$, can also be solved exactly

(d) Radiation from ro-vibrational transition

Given $k = 5.2 \times 10^5 \frac{\text{dynes}}{\text{cm}}$, $r_0 = 0.75\,\text{Å}$

Using atomic units: length $a_0 = 0.5$, energy $= \frac{e^2}{a_0}$ ...
mass $m_e$ etc.

$k$ = spring constant $= \frac{\text{Force}}{\text{Length}} = \frac{e^2}{a_0^3} \simeq 2 \times 10^6 \frac{\text{dynes}}{\text{cm}}$

$\Rightarrow k \cong \frac{1}{4}$ (a.u.) (a.u. = atomic units)

$r_0 = 1.5$ a.u

$\mu = \frac{m_p}{2} \Rightarrow \mu = \frac{m_p}{2m_e}$ a.u. $= 900$

$\Rightarrow \omega_{\text{vibration}} = \sqrt{\frac{k}{\mu}} = \frac{1}{\sqrt{4 \times 900}} = \frac{1}{60}$ a.u

$\omega_{\text{rotation}} = \frac{1}{2\mu r_0^2} = \frac{1}{2 \times 900 \times 2.25} = 2.5 \times 10^{-4}$ a.u.

Atomic unit of frequency $\omega_{\text{a.u.}} = \frac{e^2}{\hbar a_0}$

Atomic unit of wavelength $\lambda_{\text{a.u.}} = \frac{2\pi c}{\omega_{\text{a.u.}}}$

$\Rightarrow \lambda_{\text{a.u.}} = 2\pi \left(\frac{\hbar c}{e^2}\right) a_0 = (2\pi)(137)(0.5\,\text{Å}) = 430\,\text{Å}$
$= 43\,\text{nm}$

Transition
$\Delta v = 2$, $\Delta \ell = 0$

$\omega = 2\omega_{\text{vib}} \Rightarrow \lambda = \frac{\lambda_{\text{vib}}}{2} = \frac{60}{2} \lambda_{\text{a.u.}}$

$\Rightarrow \boxed{\lambda = 1290\,\text{nm}}$ infra-red

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Transition: $\Delta\bar{\nu}=0$, $\Delta l=2$

$$\omega = [(l+2)(l+2+1) - l(l+1)]\,\omega_{rot}$$
$$= (4l+6)\,\omega_{rot}$$

$$\Rightarrow \lambda = \frac{1}{4l+6}\lambda_{rot} = \frac{1}{4l+6}\,\frac{\lambda_{a.u.}}{2.5\times10^{-4}}$$

$$= \frac{1}{4l+6}\,1.7\times10^{-5}\,m = \boxed{\frac{17\,\mu m}{4l+6}}$$ far infra-red

Case $l=0$ $\lambda \cong 3\,\mu m$

(e) Deuterium molecule $\Rightarrow$ Different mass of nuclei, otherwise, everything else is the same.

Deuterium nucleus (extra neutron) $\Rightarrow m_D = 2m_p$

$$\Rightarrow \mu_{D_2} = 2\mu_{H_2}$$

Since $r_0$ and $k$ are the same for $H_2$ and $D_2$, and $l=0$ for both ground states, the difference in the binding energy must arise from difference in zero-point energy

$$\Rightarrow \Delta E_{bind} = \Delta E_{zero\text{-}point} = \tfrac{1}{2}\hbar\omega_{vib}(H_2) - \tfrac{1}{2}\hbar\omega_{vib}(D_2)$$

$$= \tfrac{1}{2}\hbar\omega_{vib}(H_2)\left(1-\sqrt{\frac{\mu_{H_2}}{\mu_{D_2}}}\right) = \frac{1}{2}\left(\frac{1}{60}\,a.u.\right)\left(1-\frac{1}{\sqrt{2}}\right)$$
$$\cong \frac{1}{400}\,a.u.$$

Aside: $1\,a.u.\ of\ energy = \frac{e^2}{a_0} = 27\,eV = (27\,eV)\left(1.6\times10^{-19}\frac{J}{eV}\right)\left(2.4\times10^{-?}\frac{kcal}{J}\right)$

$$\cong 10^{-21}\,kcal \times \left(6\times10^{23}\frac{molecules}{mole}\right)$$
$$\cong 600\ kcal/mole$$

$$\boxed{\Delta E_{bind} \cong \frac{600}{400}\,\frac{kcal}{mole} = 1.5\,\frac{kcal}{mole}}$$ in agreement

Problem 2: The ac-Stark effect

Interaction of an induced oscillating dipole with an oscillating field $\vec{E} = \vec{E}_0 \cos\omega_L t$ $\qquad \vec{E}_0 = \mathcal{E}_z \hat{e}_z$

(i) Lorentz oscillator model:




(a) The incident field will drive oscillations of the charge at frequency $\omega_L$. The eq. of motion

$$\ddot{z} + \omega_0^2 z = -e/m\, \mathcal{E}_z \cos\omega_L t$$

Go to complex amplitude $\qquad z = \mathrm{Re}(Z_0 e^{-i\omega_L t})$

$$\Rightarrow \left(-\omega_L^2 + \omega_0^2\right) Z_0 = -\frac{e}{m}\mathcal{E}_z$$

$$\Rightarrow \quad Z_0 = \left(\frac{e/m}{\omega_0^2 - \omega_L^2}\right)\mathcal{E}_z$$

Induced dipole moment oscillating at drive-frequency $\omega_L$

$$d^{(+)}_{\text{induced}} = \mathrm{Re}\left(-e Z_0 e^{-i\omega_L t}\right)$$

$$= \frac{+e^2/m}{\omega_0^2 - \omega_L^2}\,\mathcal{E}_z \cos\omega_L t$$

$$\Rightarrow \boxed{\vec{d}_{\text{ind}}(t) = \alpha\, \vec{\mathcal{E}}(t)} \qquad \boxed{\alpha = \frac{+e^2/m}{\omega_0^2 - \omega_L^2}}$$

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In the near resonance approximation:

Let $\Delta \equiv \omega_L - \omega_0$ ("detuning") $\qquad \Delta \ll \omega_0 \sim |\omega_L|$

$$\Rightarrow \omega_0^2 - \omega_L^2 = (\omega_0 + \omega_L)(\omega_0 - \omega_L) = (2\omega_0 + \Delta)(-\Delta)$$

$$\approx -2\omega_0 \Delta \quad \text{(to first order in } \Delta \ll \omega_0\text{)}$$

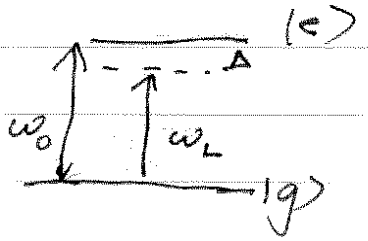
$$\therefore \quad \boxed{\alpha \approx \frac{-e^2}{2m\omega_0 \Delta}}$$

(ii) Quantum picture

(a) Given two level atom

$\Delta \ll \omega_0 \quad \Delta \ll |\omega_L|$

(ignore all other levels)




→ Effective Hamiltonian (we will derive later)

$$\hat{H} = \hat{H}_0 + \hat{H}_1$$

$\hat{H}_0 = \hat{H}_{Atom} = -\hbar\Delta\,|e\rangle\langle e|$ ("unperturbed atom")

$\hat{H}_1 = \hat{H}_{int} = -\frac{\hbar\Omega}{2}\left(|e\rangle\langle g| + |g\rangle\langle e|\right)$ ("laser interaction")

$$\Omega \equiv \frac{\langle e|\vec{d}|g\rangle \cdot \vec{E}}{\hbar}$$ "Rabi frequency"

(b) This simple 2-dimensional problem can be solve exactly! Matrix representation in basis $\{|e\rangle, |g\rangle\}$

$$H \doteq -\hbar\begin{bmatrix} \Delta & \Omega/2 \\ \frac{\Omega}{2} & 0 \end{bmatrix} = -\hbar\left(\frac{\Delta}{2}\hat{\mathbb{1}} + \frac{\Delta}{2}\hat{\sigma}_z + \frac{\Omega}{2}\hat{\sigma}_x\right)$$

$$= -\frac{\hbar\Delta}{2}\hat{\mathbb{1}} - \frac{\hbar\vec{\Omega}}{2}\cdot\vec{\sigma}$$

where $\vec{\Omega} = \Delta\vec{e}_z + \Omega\vec{e}_x$ (Generalized Rabi frequency)

$$\tilde{\Omega} \equiv |\vec{\Omega}| = \sqrt{\Omega^2 + \Delta^2}$$

$$\frac{\vec{\Omega}}{\Omega} = \cos\theta\vec{e}_z + \sin\theta\vec{e}_x$$

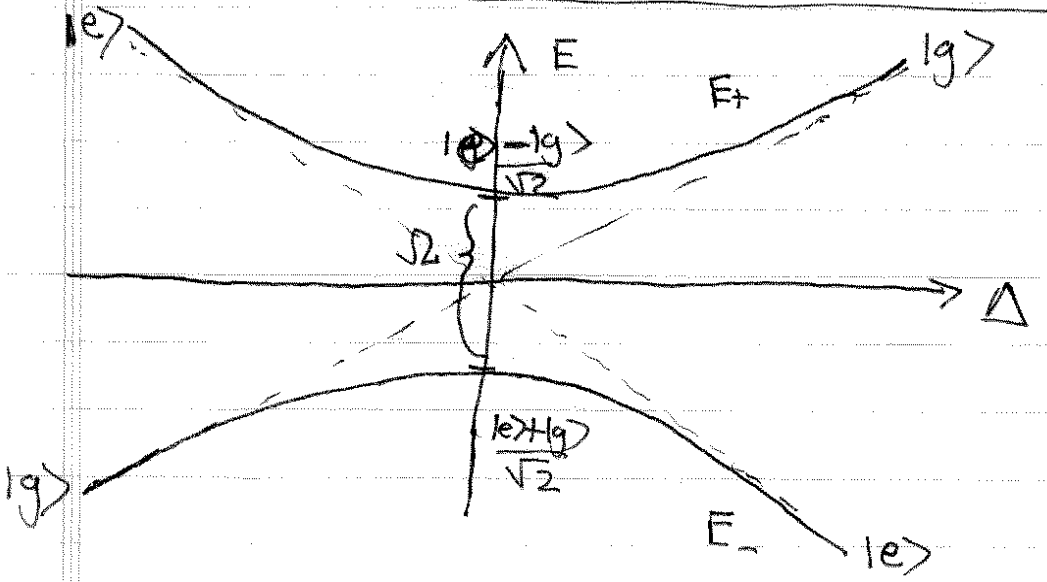
$$\tan\theta = \frac{\Omega}{\Delta}$$

$\Rightarrow$ Eigenvalues:

$$E_\pm = -\left(\frac{\hbar\Delta}{2} \pm \frac{\hbar\tilde{\Omega}}{2}\right) = -\frac{\hbar}{2}\left(\Delta \pm \sqrt{\Omega^2+\Delta^2}\right)$$

Eigenvectors: $|\pm\rangle = \cos\frac{\theta}{2}|e\rangle \pm \sin\frac{\theta}{2}|g\rangle$

$$\tan\theta = \frac{\Omega}{\Delta}$$




Typical anti-crossing behavior. At $\Delta=0$ $|e\rangle$ and $|g\rangle$ are "degenerate" in the absence of coupling. The field breaks the degeneracy into symmetric and anti-symmetric superpositions

Note for $\Delta<0$ ("red detuning") $|e\rangle$ is shifted up and $|g\rangle$ down (level repulsion)

For $\Delta>0$ ("blue detuning) the reverse occurs $\Rightarrow$ level attraction

Note: In class we saw that in static perturbation the levels always repell due to perturbation. This agrees with our result, since in the d.c. limit $\Delta$ is negative.

(c) Expansion for $\frac{\Omega}{\Delta} \ll 1$ $\left(\frac{\text{coupling matrix element}}{\text{energy level difference}}\right)$

$$E_\pm = -\frac{\hbar}{2}\left(\Delta \pm \Delta\sqrt{1+\frac{\Omega^2}{\Delta^2}}\right) \approx -\frac{\hbar}{2}\left(\Delta \pm \Delta\left(1+\frac{\Omega^2}{2\Delta^2}\right)\right)$$

$$\Rightarrow \boxed{E_+ \simeq -\hbar\Delta + \frac{\hbar\Omega^2}{4\Delta} \qquad E_- \simeq -\frac{\hbar\Omega^2}{4\Delta}}$$

Lowest non-vanishing perturbation is second order in $\Omega$

(d) Using perturbation theory $\hat{H}_1 = -\frac{\hbar\Omega}{2}(|e\rangle\langle g| + h.c.)$

0th order $E_e^{(0)} = -\hbar\Delta$ $|e\rangle$ $\qquad E_g^{(0)} = 0$ $|g\rangle$

1st order $E_e^{(1)} = \langle e|\hat{H}_1|e\rangle = 0 \qquad E_g^{(1)} = \langle g|\hat{H}_1|g\rangle = 0$

2nd order $E_e^{(2)} = \frac{|\langle g|\hat{H}_1|e\rangle|^2}{E_e^{(0)} - E_g^{(0)}} = \frac{\frac{\hbar^2\Omega^2}{4}}{-\hbar\Delta} = -\frac{\hbar\Omega^2}{4\Delta}$

$E_g^{(2)} = \frac{|\langle e|\hat{H}_1|g\rangle|^2}{E_g^{(0)} - E_e^{(0)}} = \frac{\frac{\hbar\Omega^2}{4}}{\hbar\Delta} = \frac{\hbar\Omega^2}{4\Delta}$

Thus to second order

$$E_e = E_e^{(0)} + E_e^{(2)} = -\hbar\Delta - \frac{\hbar\Omega^2}{4\Delta} \quad \checkmark$$

$$E_g = E_g^{(0)} + E_g^{(2)} = +\frac{\hbar\Omega^2}{4\Delta} \quad \checkmark$$

as in (6)

Mean dipole: (Assume atm starts in ground state)

To first order: $|\tilde{\phi}_g\rangle = |g\rangle + |e\rangle\frac{\langle e|\hat{H}_1|g\rangle}{E_g^{(0)} - E_e^{(1)}}$

$= |\phi_g^{(0)}\rangle + |\phi_g^{(1)}\rangle$

$\Rightarrow |\tilde{\phi}_g\rangle = |g\rangle - \frac{\Omega}{2\Delta}|e\rangle$ (unnormalized)

$$\langle\vec{d}\rangle = \frac{\langle\tilde{\phi}_g|\vec{d}|\tilde{\phi}_g\rangle}{\langle\tilde{\phi}_g|\tilde{\phi}_g\rangle} = \frac{-\frac{1}{2\Delta}\left(\Omega^*\langle e|\vec{d}|g\rangle + \Omega\langle g|\vec{d}|e\rangle\right)}{1 + \frac{\Omega^2}{4\Delta^2}}$$

$\frac{\Omega^2}{4\Delta^2}$ → neglect

$\Rightarrow$ To lowest order in $\Omega = \frac{\langle e|\vec{d}|g\rangle}{\hbar} \cdot \vec{\mathcal{E}}$

$$\boxed{\langle\vec{d}\rangle = -\frac{|\langle e|\vec{d}|g\rangle|^2}{\hbar\Delta}\vec{\mathcal{E}} = \alpha\vec{\mathcal{E}}}$$

Now

$$\boxed{E_g^{(2)} = \frac{\hbar\Omega^2}{4\Delta} = \frac{|\langle e|\vec{d}|g\rangle|^2}{4\hbar\Delta}|\vec{\mathcal{E}}|^2 = -\frac{1}{4}\alpha|\vec{\mathcal{E}}|^2}$$

as in the classical calculation (6) ✓

(e) Oscillator strength

$$f \equiv \frac{\alpha_q}{\alpha_c} \simeq \left(\frac{|\langle e|\vec{d}|g\rangle|^2}{\hbar\Delta}\right)\left(\frac{2m\omega_0 \Delta}{e^2}\right)$$

$$= |\langle e|z|g\rangle|^2 \left(\frac{2m\omega_0}{\hbar}\right)$$

$$\boxed{f = \frac{|\langle e|z|g\rangle|^2}{(\Delta z)^2_{SHO}}} \quad \text{where} \quad (\Delta z)_{SHO} = \frac{\hbar}{2m\omega_0}$$

For a multi-level atom with resonances $\{\omega_i\}$

$$\alpha = \sum_i f(\omega_i)\,\alpha(\omega_i)$$

the oscillator strength satisfies the "sum rule"

$$\sum_i f(\omega_i) = Z \text{ (atomic \#)}$$

For Hydrogen and the alkalies, the majority of the oscillator strength lies in the first $s \to p$ transition. Thus, if the perturbation is far from any resonance, this transition will dominate.