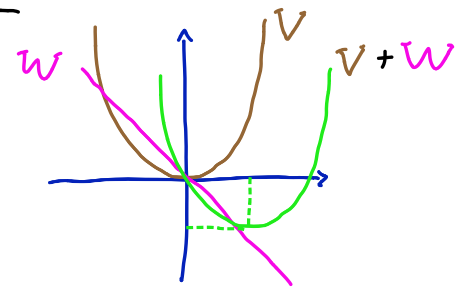
Charged oscillator in electric field



$$H_{\mathcal{E}} = \frac{P^2}{2m} + \underbrace{\frac{1}{2}m\omega^2 X^2}_{V} - \underbrace{q\mathcal{E}X}_{W}$$

$x_0 = q\mathcal{E}/m\omega^2 \qquad E_0 = -q^2\mathcal{E}^2/2m\omega^2$

$$H = \frac{P^2}{2m} + \frac{1}{2}m\omega^2(X - x_0)^2 + E_0$$

Spectrum $E_n = (n + \frac{1}{2})\hbar\omega + E_0$

Wavefunctions $\varphi_n^{\mathcal{E}}(x) = \varphi_n(x - x_0)$

Dielectric Susceptibility

dipole moment $D = qX$

$$\langle D\rangle_{\mathcal{E}} = q\langle\varphi_n^{\mathcal{E}}|X|\varphi_n^{\mathcal{E}}\rangle = q\int dx\ \ x|\varphi_n(\underbrace{x - x_0}_{u})|^2$$

$$= q\int du\ \ u|\varphi_n(u)|^2 + \frac{q^2\mathcal{E}}{m\omega^2}\int du\ |\varphi_n(u)|^2$$

$$= \frac{q^2\mathcal{E}}{m\omega^2}$$

$$\chi = \frac{\langle D\rangle_{\mathcal{E}}}{\mathcal{E}} = \frac{q^2}{m\omega^2} = \frac{q^2}{k}$$

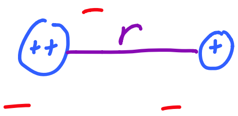
Energy Shift

electric energy $\quad -q\mathcal{E}x_0 = -\dfrac{q^2\mathcal{E}^2}{m\omega^2} = 2E_0$

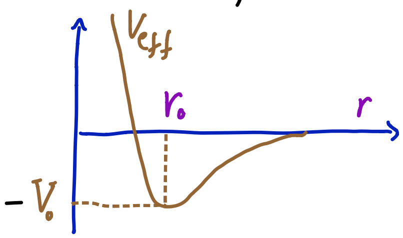
elastic energy $\quad \frac{1}{2}kx_0^2 = -E_0 = +\dfrac{q^2\mathcal{E}^2}{2m\omega^2}$

net energy $\quad -q\mathcal{E}x_0 + \frac{1}{2}kx_0^2 = E_0$

Applications (Molecular spectroscopy)



Interatomic potential $V_{eff}(r) = E_0(r) + \frac{Z_1 Z_2 e^2}{r}$



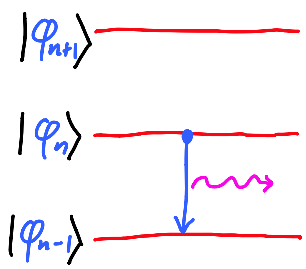
$\uparrow$ electronic ground state, fixed nuclei

rotational, vibrational motion decouples

Let $\omega = \sqrt{V''(r_0)/m}$, $E_n = (n+\frac{1}{2})\hbar\omega$ relative to $-V_0$

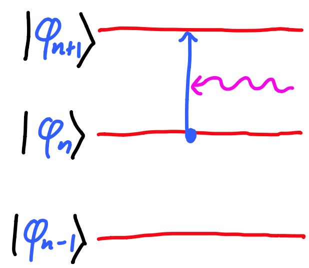
Infrared Absorption

Heteropolar molecule $\Rightarrow$ $D(r) = d_0 + d_1(r - r_0)$



emission

$\langle\varphi_{n-1}|D(r)|\varphi_n\rangle$



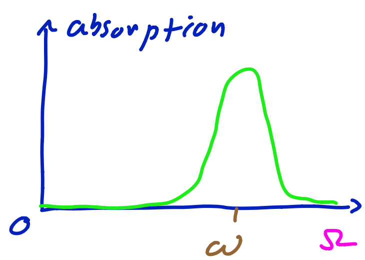
absorption

$\langle\varphi_{n+1}|D(r)|\varphi_n\rangle$

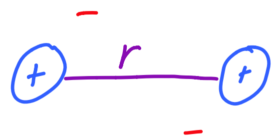
Bohr frequency

$$\frac{E_{n\pm1} - E_n}{\hbar} = \pm\omega$$

only $\omega = |\pm\omega|$ observed



Raman Effect



homopolar molecule $\Rightarrow D = 0$

no infrared signal

irradiate with optical radiation freq. $\Omega \gg \omega$

induced dipole moment $D(t) = \chi \, \mathcal{E}_0 e^{i\Omega t}$

Note: $\chi = \chi(r)$

Vibration $r \longrightarrow r_0 + \delta \cos(\omega t) \Rightarrow \chi = \chi_0 + \delta \chi' \cos(\omega t)$

$$D(t) = \underset{\sim e^{i\Omega t}}{\underset{\uparrow}{D_0(t)}} + \delta \chi' \mathcal{E}_0 e^{i(\Omega \pm \omega)t}$$