Quantum Mechanics

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Electromagnetic Interaction

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Electromagnetic Interaction

The most common way of studying a quantum system is to probe it using electromagnetic waves. The Hamiltonian of an electron interacting with an electromagnetic field is

$$H = \frac{\left(p + \frac{e}{c}A\right)^2}{2m} - e\phi$$

where A, ϕ are the vector and scalar potentials, respectively. Now,

$$\left(p + \frac{e}{c}A\right)^2 = p^2 + \frac{e}{c}p \cdot A + \frac{e}{c}A \cdot p + \left(\frac{e}{c}A\right)^2$$

and

$$p \cdot A\psi = -i\hbar\partial_i(A_i\psi) = -i\hbar\psi\partial_i A_i - i\hbar A_i\partial_i\psi = -i\hbar\psi\nabla \cdot A + A \cdot p\psi$$

In the Coulomb Gauge

$$\nabla \cdot A = 0$$

Thus,

$$H = \frac{p^2}{2m} - e\phi + \frac{e}{mc}A \cdot p + \frac{e^2}{2mc^2}A^2$$

Interaction Potential

The last term is generally negligible. Thus,

$$H = H_0 + \frac{e}{mc} A \cdot p$$

where

$$H_0 = \frac{p^2}{2m} - e\phi$$

For a system in a radiation field

$$A(x,t) = A_0 e^{i(k\cdot x - \omega t)} + A_0 e^{-i(k\cdot x - \omega t)}$$

The time dependent potential is

$$V(t) = \frac{e}{mc} A \cdot p = \frac{eA_0}{mc}(\varepsilon \cdot p)\left[e^{i(k\cdot x - \omega t)} + e^{-i(k\cdot x - \omega t)}\right]$$

where ε is the polarization vector.

Absorption Cross Section

The transition rate with this harmonic perturbation is

$$w_{i\to[n]} = \frac{2\pi}{\hbar}\frac{e^2}{m^2c^2}|A_0|^2\left|\langle n|(\varepsilon\cdot p)e^{ik\cdot x}|i\rangle\right|^2\delta(E_n - E_i - \hbar\omega)$$

The absorption cross section is defined as the energy per unit time absorbed by the atom divided by the energy flux of the radiation field which is

$$u = \frac{1}{2\pi}\frac{\omega^2}{c^2}|A_0|^2$$

Thus,

$$\sigma_{abs} = \frac{w_{i\to[n]}\hbar\omega}{uc} = \left(\frac{2\pi}{m}\right)^2\left(\frac{e^2}{\hbar c}\right)\frac{\hbar}{\omega}\left|\langle n|(\varepsilon\cdot p)e^{ik\cdot x}|i\rangle\right|^2\delta(E_n - E_i - \hbar\omega)$$

Electric Dipole Approximation

If the wavelength of the radiation field is much longer than the system's dimension,

$$e^{ik\cdot x} = 1 + i\frac{\omega}{c}\hat{k}\cdot x + \cdots$$

The matrix element may be cast as

$$\langle n \big| (\varepsilon \cdot p) e^{ik\cdot x} \big| i \rangle \approx \varepsilon \cdot \langle n|p|i\rangle$$

Now,

$$[x_i\,, H_0] = \left[x_i\,, \frac{p^2}{2m} - e\phi(x)\right] = \left[x_i\,, \frac{p^2}{2m}\right] = \sum_{k=1}^{3}\left(\frac{p_k}{2m}[x_i, p_k] + [x_i, p_k]\frac{p_k}{2m}\right)$$

$$= \sum_{k=1}^{3}\frac{p_k}{m} i\hbar\delta_{ik} = i\hbar\frac{p_i}{m}$$

Thus,

$$\langle n|p|i\rangle = \frac{m}{i\hbar}\langle n|[x, H_0]|i\rangle = \frac{m}{i\hbar}\langle n|xH_0 - H_0x|i\rangle = \frac{m}{i\hbar}(E_i - E_n)\langle n|x|i\rangle$$

Because the term ex is the electric dipole, this is called the electric dipole approximation.

Spherical Harmonics Representations

Electromagnetic waves are transverse. The polarization vector ε are perpendicular to the wave vector k. If we take the direction of propagation as the $z-$ axis, then ε must lie on the $xy-$ plane. The matrix element $\langle n|(\varepsilon \cdot p)e^{ik\cdot x}|i\rangle$ therefore carries no $\langle n|z|i\rangle$ term.

The matrix elements $\langle n|x|i\rangle$ and $\langle n|y|i\rangle$ may be evaluated using spherical harmonics

$$x = \sqrt{\frac{8\pi}{3}}\, r\left(\frac{Y_{1,-1} - Y_{11}}{2}\right)\ ; \quad y = \sqrt{\frac{8\pi}{3}}\, r\left(\frac{Y_{1,-1} + Y_{11}}{2}\right)$$

So $\langle n|\vec{x}|i\rangle$ comprise terms of the form

$$\langle nl|r|n'l'\rangle\langle nlm|Y_{LM}|n'l'm'\rangle$$

The angular part may be evaluated using the Triple-Y formula

$$\int Y_{jm}^{*} Y_{j_1 m_1} Y_{j_2 m_2} d\Omega = \sqrt{\frac{(2j_1+1)(2j_2+1)}{4\pi(2j+1)}}\langle j_1 j_2 m_1 m_2|j_1 j_2 j m\rangle\langle j_1 j_2 00|j_1 j_2 j 0\rangle$$

Selection Rules

The Clebsch-Gordan coefficients vanish unless $m' = m_1 + m_2$. Since the quantum number M in the middle Y are only ± 1. The magnetic quantum numbers of the initial and final states must therefore differ only by ± 1. The first selection rule is then

$$\Delta m = m_f - m_i = \pm 1$$

Since the middle Y has $L = 1$, then the final state, which corresponds to the total angular momentum state in the triple-Y formula, must have a value of either $l - 1, l,$ or $l + 1.$

The matrix element $\langle n | (\varepsilon \cdot p) e^{ik \cdot x} | i \rangle$ is scalar. It must therefore be invariant under reflection. The parity of the spherical harmonics is $(-1)^l$. Since the middle Y has $L = 1,$ The matrix element would be even parity only if the initial and final states have angular momentum quantum numbers that differ by 1. We then have the second selection rule in the electric dipole approximation

$$\Delta l = l_f - l_i = \pm 1$$

No radiative transitions are allowed unless both selection rules are satisfied.

Thomas-Reiche-Kuhn Sum Rule

Let us consider the commutator $\left[x,[x,H_0]\right]$ and let $|i\rangle$ be eigenkets of H_0. Then

$$\langle i|\left[x,[x,H_0]\right]|i\rangle = \langle i|[x, xH_0 - H_0x]|i\rangle = \langle i|x^2H_0 - 2xH_0x + H_0x^2|i\rangle$$

$$= 2E_i\langle i|x^2|i\rangle - 2\langle i|xH_ox|i\rangle = 2E_i\sum_n\langle i|x|n\rangle\langle n|x|i\rangle - 2\sum_n\langle i|xH_o|n\rangle\langle n|x|i\rangle$$

$$= 2\sum_n(E_i - E_n)\,\langle i|x|n\rangle\langle n|x|i\rangle = \sum_n 2\hbar\omega_{in}|\langle n|x|i\rangle|^2$$

On the other hand,

$$[x\,,H_0] = i\hbar\frac{p}{m}$$

$$\left[x,[x,H_0]\right] = \frac{i\hbar}{m}[x\,,p] = -\frac{\hbar^2}{m}$$

Then,

$$\sum_n 2\hbar\omega_{in}|\langle n|x|i\rangle|^2 = -\frac{\hbar^2}{m}$$

Total Absorption Cross Section

The total absorption cross section is then

$$\sigma_{Total} = \int \sigma_{abs}(\omega)\, d\omega = \left(\frac{e^2}{\hbar c}\right)\left(\frac{2\pi}{m}\right)^2 \int \frac{\hbar}{\omega} \left|\langle n|(\varepsilon \cdot p) e^{ik\cdot x}|i\rangle\right|^2 \delta(E_n - E_i - \hbar\omega) d\omega$$

$$\approx \left(\frac{e^2}{\hbar c}\right)\left(\frac{2\pi}{m}\right)^2 \sum_n \frac{1}{\omega_{ni}} |\varepsilon \cdot \langle n|p|i\rangle|^2 = \left(\frac{e^2}{\hbar c}\right)\left(\frac{2\pi}{m}\right)^2 \sum_n \frac{1}{\omega_{ni}} \left|\varepsilon \cdot \frac{m}{i\hbar}(E_i - E_n)\langle n|x|i\rangle\right|^2$$

Without loss of generality, we may take the polarization to be along the x −axis. Then

$$\sigma_{Total} = \left(\frac{e^2}{\hbar c}\right)\left(\frac{2\pi}{m}\right)^2 \sum_n m^2 \omega_{ni}\, |\langle n|x|i\rangle|^2 = 4\pi^2 \alpha \frac{\hbar}{2m} = \frac{2\pi^2 \hbar \alpha}{m}$$

This is the same as the classical value.