Deriving the matrix element

Recall that the unperturbed Hamiltonian is:

$$\hat{H}_o = \frac{\hat{p}^2}{2m} + V(\bar{r})$$

In the presence of (weak) light, the Hamiltonian is perturbed:

$$\hat{H} = \hat{H}_o + \hat{H}'$$

To determine the perturbation, recall that Force is given by the time rate of change of the momentum:

$$\bar{F} = \frac{d\bar{P}}{dt}$$

where $\bar{P}$ is the classical momentum. In the presence of an electric field, this force becomes:

$$\bar{F} = \frac{d\bar{P}}{dt} + e\bar{E}$$

where $\bar{E}$ is the electric field. Assuming no OTHER charge is present, then Φ = const and

$$\bar{E} = -\frac{\partial\bar{A}}{\partial t} \implies \bar{F} = \frac{d\bar{P}}{dt} - e\frac{\partial\bar{A}}{\partial t}$$

where $\bar{A}$ is the vector potential. We can rewrite the total force as a time derivative of a "Canonical" momentum:

$$\bar{F} = \frac{d}{dt}(\bar{P} - e\bar{A}) = \frac{d}{dt}\bar{P}_c$$

We can treat this canonical momentum as a perturbed version of the original momentum, substituting for $\bar{P}$ in the expression for $\hat{H}$:

$$\hat{H} \simeq \frac{1}{2m}(\bar{P} - e\bar{A})^2 + V(\bar{r})$$

We wish to find specifically what $\hat{H}'$ is. This requires a bit of math:

$$\hat{H} = \frac{1}{2m}\left(p^2 - e\bar{P}\cdot\bar{A} - e\bar{A}\cdot\bar{P} + A^2 \right) + V(\bar{r})$$

Since we are only considering weak perturbations, we can safely eliminate terms to order A^2 or higher, hence:

$$\hat{H} \simeq \frac{p^2}{2m} + V(\bar{r}) - e\bar{P}\cdot\bar{A} - e\bar{A}\cdot\bar{P}$$

From this expression, it is straight forward to see that:

$$\hat{H}' = \left[-e\bar{P}\cdot\bar{A} - e\bar{A}\cdot\bar{P} \right] \frac{1}{2m}$$

Next, we take advantage of an important property of the Coulomb gauge and Quantum mechanics:

$$\boxed{\left[P_i, F(\bar{x}) \right] = -i\hbar \frac{\partial}{\partial x_i} F(\bar{x})} \Rightarrow \left[\bar{P}, \bar{A} \right] = -i\hbar \bar{\nabla}\cdot\bar{A} = 0$$

Thus $\bar{p}$ & $\bar{A}$ commute. The perturbation becomes:

$$\hat{H}' = -\frac{e}{m_0}\bar{P}\cdot\bar{A} = -\frac{e}{m_0}\bar{A}\cdot\bar{P}$$

Next, for simplicity, let us choose $\bar{A}$ to be a simple plain wave, ie $\bar{A} = \hat{e}\,\frac{A_0}{2}\,e^{i\bar{k}_{op}\cdot\bar{r} - i\omega t}$

It follows that:

$$H' = -\frac{eA_0}{2m} e^{i\bar{k}_{op}\cdot\bar{r} - i\omega t}\,\hat{e}\cdot\bar{P}$$

Finally, we want to find a specific matrix element, ie $\hat{H}'_{ba}$ which amounts to taking an outer product w/ $|a\rangle$ and $|b\rangle$:

$$H'_{ba} = -\frac{eA_0}{2m} e^{-i\omega t}\,\hat{e}\,\langle b| e^{i\bar{k}_{op}\cdot\bar{r}}\,\bar{P}\,|a\rangle$$

let us make the approximation that $\bar{k}_{op}\cdot\bar{r} \sim 0 \Rightarrow e^{i\bar{k}_{op}\cdot\bar{r}}$ varies very slowly

$$\Rightarrow \boxed{H'_{ba} \approx -\frac{eA_0}{2m_0} e^{i(\bar{k}_{op}\cdot\bar{r} - \omega t)}\,\hat{e}\cdot\langle b|\bar{P}|a\rangle} = -\frac{e}{m_0}\bar{A}\cdot\bar{P}$$

Dipole Approximation

We found that the matrix element $\mathcal{H}'_{ba}$ is given by:

$$\mathcal{H}'_{ba} = -\frac{eA_0}{2m_0} e^{i(\bar{k}_{op}\cdot\bar{r}-\omega t)} \hat{e}\cdot\langle b|\bar{p}|a\rangle$$

We wish to find an expression for $\mathcal{H}'_{ba}$ that depends on more intuitive quantities than $\bar{p}$. To do so, we first consider the definition of $\bar{p}$ as viewed using the Heisenberg picture of QM:

$$\bar{p} = m_0\bar{v} = m_0\frac{d\bar{r}}{dt}$$

where $\bar{r}$ is the position operator. The Heisenberg picture tells us:

$$\frac{\partial\bar{r}}{\partial t} = \frac{1}{i\hbar}[\bar{r},\hat{\mathcal{H}}]$$

Since we are considering only the classical position/momentum, we use the unperturbed Hamiltonian $\hat{\mathcal{H}}_0$:

$$\frac{\partial\bar{r}}{\partial t} = \frac{1}{i\hbar}[\bar{r},\hat{H}_0] = \frac{1}{i\hbar}[\bar{r}\hat{H}_0 - \hat{H}_0\bar{r}]$$

Thus it follows that:

$$\langle b|\bar{p}|a\rangle = m\langle b|\frac{\partial\bar{r}}{\partial t}|a\rangle = \frac{m}{i\hbar}\langle b|\bar{r}\hat{H}_0 - \hat{H}_0\bar{r}|a\rangle$$

$$= \frac{m}{i\hbar}[E_a\langle b|\bar{r}|a\rangle - E_b\langle b|\bar{r}|a\rangle] \quad \text{since} \quad \left\{\begin{array}{l}\hat{H}_0|a\rangle = E_a|a\rangle \\ \langle b|\hat{H}_0 = E_b\langle b|\end{array}\right.$$

$$= \frac{m}{i\hbar}(E_a - E_b)\langle a|\bar{r}|b\rangle$$

Note that $E_b - E_a = \hbar\omega$ (from Fermi's golden rule?) Thus:

$$\langle b|\bar{p}|a\rangle = +\frac{m\omega}{i}\langle b|\bar{r}|a\rangle = -im\omega\langle b|\bar{r}|a\rangle$$

Thus the matrix element is:

$$\mathcal{H}'_{ba} = -\frac{ie\omega A_0}{2} e^{i(\bar{k}_{op}\cdot\bar{r}-\omega t)} \hat{e}\cdot\langle b|\bar{r}|a\rangle$$

Notice that in the absence of an additional potential,

$$\bar{E} = -\frac{\partial \bar{A}}{\partial t} = i\omega \bar{A}$$

Thus it follows that

$$\boxed{\mathcal{H}'_{ba} \simeq -e\bar{E} \cdot \langle b|\bar{r}|a\rangle = -e\bar{E} \cdot \bar{r}_{ba}}$$