

The mathematical derivation of the Franck–Condon principle was sloppy in the lecture (sorry). The interaction energy between the oscillating x -polarized electric field and electrical charges in a molecule consists of two terms,

$$\hat{H}^{(1)} = E \cos(\omega t) \left(\sum_i -e\hat{x}_i + \sum_I Z_I e\hat{x}_I \right), \quad (1)$$

where E is the field amplitude, ω is the frequency of light, $-e$ is the electric charge of electron, x_i is the x coordinate of the i th electron, Z_I is the atomic number of the I th nucleus ($Z_I e$ is its electric charge), and x_I is the x coordinate of the I th nucleus.

The transition dipole moment (the integral in the equation below), which is derivable from the first-order time-dependent perturbation theory with the above perturbation operator, therefore, has two terms, too:

$$I_{m \leftarrow n} \propto E^2 \left| \int \Psi_m^* \left(\sum_i -e\hat{x}_i + \sum_I Z_I e\hat{x}_I \right) \Psi_n d\tau \right|^2, \quad (2)$$

which is why it can be divided into two separate integrals:

$$\begin{aligned} & \int \Psi_m^* \left(\sum_i -e\hat{x}_i + \sum_I Z_I e\hat{x}_I \right) \Psi_n d\tau \\ &= \int \psi_m^{e*} \psi_m^{v*} \left(\sum_i -e\hat{x}_i + \sum_I Z_I e\hat{x}_I \right) \psi_n^e \psi_n^v d\tau_e d\tau_v \\ &= \int \psi_m^{e*} \left(\sum_i -e\hat{x}_i \right) \psi_n^e d\tau_e \int \psi_m^{v*} \psi_n^v d\tau_v + \int \psi_m^{e*} \psi_n^e d\tau_e \int \psi_m^{v*} \left(\sum_I Z_I e\hat{x}_I \right) \psi_n^v d\tau_v, \end{aligned} \quad (3)$$

where the Born–Oppenheimer separation of the electronic ($'e'$) and nuclear ($'v'$) degrees of freedom has been made. Operators \hat{x}_i act only on the electronic wave functions ψ^e and integrated over electronic coordinates τ_e , while operators \hat{x}_I act on the nuclear wave functions ψ^v and integrated over nuclear coordinates τ_v .

In the lecture, the two components of the operator were collectively referred to as $'\hat{x}'$, which was incorrect and did not explain why the integral splits into two terms.