

CHM 502 - 9 - Electronic Transitions

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Let's now turn our attention to electronic states and light-driven transitions between them.

1 The Born-Oppenheimer approximation

For molecules, all information is contained in the wavefunction Ψ , which is a solution to the time-independent Schrödinger equation:

$$\hat{H}\Psi(\vec{r}, \vec{R}) = E\Psi(\vec{r}, \vec{R}) \quad (1)$$

where \vec{r} stands collectively for the spatial and spin coordinates of the n electrons in the molecule, and \vec{R} denotes collectively the positions of all N nuclei in the molecule. The total Hamiltonian for the molecule is:

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{eN} + \hat{V}_{ee} + \hat{V}_{NN} \equiv \hat{T}_N + \hat{H}^{el} \quad (2)$$

where \hat{T} terms represent kinetic energy operators for movement of the electrons and nuclei. \hat{V} terms represent potential energy operators that derive from Coulomb interaction energies between nuclei and electrons, among electrons, and among nuclei. e labels electronic degrees of freedom and N represents nuclear degrees of freedom. We therefore have:

$$\hat{T}_N = - \sum_i \frac{\hbar^2}{2M_i} \nabla_{R_i}^2 \quad (3)$$

$$\hat{T}_e = - \sum_i \frac{\hbar^2}{2m_e} \nabla_{r_i}^2 \quad (4)$$

$$\hat{V}_{e,N} = - \sum_{i,j} \frac{Z_i \cdot e^2}{4\pi\epsilon_0 |\vec{R}_i - \vec{r}_j|} \quad (5)$$

$$\hat{V}_{e,e} = - \sum_{i,j} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} \quad (6)$$

$$\hat{V}_{N,N} = - \sum_{i,j} \frac{Z_i \cdot Z_j \cdot e^2}{4\pi\epsilon_0 |\vec{R}_i - \vec{R}_j|} \quad (7)$$

where M_i is the mass and Z_i is the nuclear charge of the i^{th} nucleus, m_e is the electron mass, and e is the electron charge. $\nabla_{r_i}^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$ is the Laplacian operator.

Eqn. 2 is therefore a $(3n + 3N)$ -dimensional second order partial differential equation which is not easily solved.

Because the masses of the nuclei are much larger than those of the electrons, the nuclei move slowly compared to the electrons. It is usually (but not always!) a good approximation to assume that the energy of the system due to the motion of electrons can be determined accurately with the nuclei held fixed at each possible set of nuclear positions. In other words, it is assumed that the electrons adjust adiabatically to small or slow changes in the nuclear geometry. This approximation and its consequences were first examined by Born and Oppenheimer (Ann. Physik **84**, 457 (1927)).

Within the Born-Oppenheimer approximation, the total wavefunction is separable

$$\Psi(\vec{r}, \vec{R}) = \Psi^{el}(\vec{r}; \vec{R}) \cdot \Psi^{nuc}(\vec{R}) \quad (8)$$

into a nuclear part Ψ^{nuc} that depends only upon the nuclear coordinates \vec{R} and an electronic part Ψ^{el} that depends on the electronic coordinates \vec{r} , but only *parametrically* on \vec{R} .

Ψ^{el} is the solution of the electronic eigenvalue equation

$$\hat{H}^{el} \Psi^{el}(\vec{r}; \vec{R}) = E^{el}(\vec{R}) \Psi^{el}(\vec{r}; \vec{R}) \quad (9)$$

where $E^{el}(\vec{R})$ is the potential energy surface, or in the case of a diatomic molecule, the potential energy curve of the molecule in a particular electronic state.

Substituting the Born-Oppenheimer wavefunction into Eqn. 2, we find:

$$\hat{H}\Psi = [\hat{T}_N + \hat{H}_{el}] \Psi^{el} \Psi^{nuc} = E \Psi^{el} \Psi^{nuc} \quad (10)$$

$$= - \sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 \Psi^{el} \Psi^{nuc} + \hat{H}^{el} \Psi^{el} \Psi^{nuc} \quad (11)$$

$$\simeq - \Psi^{el} \sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 \Psi^{nuc} + E^{el}(\vec{R}) \Psi^{el} \Psi^{nuc} \quad (12)$$

where we have implicitly made the assumption that

$$\nabla_i^2 \Psi^{el} \Psi^{nuc} \simeq \Psi^{el} \nabla_i^2 \Psi^{nuc} \quad (13)$$

which comes down to neglecting “non-adiabatic” interactions. This is usually justified, except when the electronic wavefunction changes rapidly with the nuclear coordinates. This can happen, for example, in the regions where two states interfere with one another near a curve crossing or conical intersection.

In any event, we can continue on to write

$$\hat{H}\Psi = - \cancel{\Psi^{el}} \sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 \Psi^{nuc} + E^{el}(\vec{R}) \cancel{\Psi^{el}} \Psi^{nuc} = E \cancel{\Psi^{el}} \Psi^{nuc} \quad (14)$$

$$\rightarrow \boxed{\left[- \sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 + E^{el}(\vec{R}) - E \right] \Psi^{nuc}(\vec{R}) = 0} \quad (15)$$

This last expression is an eigenvalue equation for the nuclear motion, where $E^{el}(\vec{R})$ acts as the potential in which the nuclei move.

This approximation gives us a straightforward way to separately determine the electronic and nuclear wavefunctions:

- First, we solve Eqn. 9 for fixed nuclear coordinates \vec{R} and repeat this process to map out the $E^{el}(\vec{R})$ surfaces for each electronic configuration. In practice, one uses a quantum chemistry software package to do this.
- Then, we use these $E^{el}(\vec{R})$ surfaces as our potential energy curves and solve Eqn. 15 to find the vibrational nuclear wavefunctions for each electronic state. The harmonic oscillator approximation is often assumed near a minimum on each $E^{el}(\vec{R})$ surface.

For the sake of completeness, we also note here that the nuclear wavefunction is in fact composed of both vibrational and nuclear wavefunctions, which we usually take to be separable, ignoring any vibration-rotation interaction $\Psi^{nuc} = \Psi^{vib}\Psi^{rot}$.

2 Vibronic transitions and the Franck-Condon principle

Let's now think about transitions between electronic states, which can also be accompanied by a change in the vibrational wavefunction. We'll first consider this the usual way, in the context of Fermi's Golden Rule, which tells us that the probability of making a transition between state Ψ_i and state Ψ_f is given by:

$$\Gamma_{fi} \propto |\langle \Psi_f | \hat{\mu} | \Psi_i \rangle|^2 \quad (16)$$

Within the Born-Oppenheimer approximation, and neglecting the rotational part of the nuclear wavefunction, we can write

$$|\Psi\rangle = |\Psi^{vib}(\vec{R})\rangle |\Psi^{el}(\vec{r}; \vec{R})\rangle \quad (17)$$

For the permanent dipole moment operator $\hat{\mu}$ we must now consider contributions from both nuclear and electron charges:

$$\hat{\mu} = \sum_{i=1}^N Z_i \cdot \vec{R}_i + \sum_{i=1}^n e \cdot \vec{r}_i \equiv \hat{\mu}_N(\vec{R}) + \hat{\mu}_e(\vec{r}) \quad (18)$$

Let's now evaluate the matrix element:

$$\langle \Psi_f | \hat{\mu} | \Psi_i \rangle = \langle \Psi_f^{vib} | \langle \Psi_f^{el} | [\hat{\mu}_N + \hat{\mu}_e] | \Psi_i^{el} \rangle | \Psi_i^{vib} \rangle \quad (19)$$

$$= \langle \Psi_f^{vib} | \langle \Psi_f^{el} | \hat{\mu}_N | \Psi_i^{el} \rangle | \Psi_i^{vib} \rangle + \langle \Psi_f^{vib} | \langle \Psi_f^{el} | \hat{\mu}_e | \Psi_i^{el} \rangle | \Psi_i^{vib} \rangle \quad (20)$$

Let's evaluate the two components of this last expression separately. First, the transition dipole matrix element arising from the nuclear contribution to the permanent dipole moment:

$$\langle \Psi_f^{vib}(\vec{R}) | \langle \Psi_f^{el}(\vec{r}; \vec{R}) | \hat{\mu}_N(\vec{R}) | \Psi_i^{el}(\vec{r}; \vec{R}) \rangle | \Psi_i^{vib}(\vec{R}) \rangle \quad (21)$$

$$= \int \int d\vec{r} d\vec{R} \Psi_f^{vib}(\vec{R}) \cdot \Psi_f^{el}(\vec{r}; \vec{R}) \cdot \hat{\mu}_N(\vec{R}) \cdot \Psi_i^{el}(\vec{r}; \vec{R}) \cdot \Psi_i^{vib}(\vec{R}) \quad (22)$$

$$= \int d\vec{R} \Psi_f^{vib}(\vec{R}) \cdot \hat{\mu}_N(\vec{R}) \cdot \Psi_i^{vib}(\vec{R}) \int d\vec{r} \underbrace{\Psi_f^{el}(\vec{r}; \vec{R}) \cdot \Psi_i^{el}(\vec{r}; \vec{R})}_{=0} = 0 \quad (23)$$

Here, we were able to factor out the electronic component of the wavefunction into a separate integral depending only on the electronic coordinates \vec{r} . For $f \neq i$, the two electronic wavefunctions are eigenfunctions of the same electronic Hamiltonian and are therefore orthogonal. So this term does not contribute!

Let's now consider the transition dipole matrix element arising from the second term of Eqn. 20, the electronic contribution to the permanent dipole moment:

$$\langle \Psi_f^{vib}(\vec{R}) | \langle \Psi_f^{el}(\vec{r}; \vec{R}) | \hat{\mu}_e(\vec{r}) | \Psi_i^{el}(\vec{r}; \vec{R}) \rangle | \Psi_i^{vib}(\vec{R}) \rangle \quad (24)$$

$$\equiv \langle \Psi_f^{vib}(\vec{R}) | D^{el}(\vec{R}) | \Psi_i^{vib}(\vec{R}) \rangle \quad (25)$$

where we define $D^{el}(\vec{R}) = \langle \Psi_f^{el} | \hat{\mu}_e | \Psi_i^{el} \rangle$ as the electronic transition dipole moment. This quantity tells us whether the transition between two electronic configurations is allowed, and is easily evaluated using group theory. To treat the dependence of $D^{el}(\vec{R})$ on the nuclear coordinates, we perform yet another Taylor expansion:

$$D^{el}(\vec{R}) = D^{el}(\vec{R}_{eq}) + \left. \frac{dD^{el}(\vec{R})}{d\vec{R}} \right|_{\vec{R}_{eq}} (\vec{R} - \vec{R}_{eq}) + \dots \quad (26)$$

We'll perform a severe truncation this time, and assume that the electronic transition dipole varies very little near equilibrium, and therefore:

$$D^{el}(\vec{R}) \simeq D^{el}(\vec{R}_{eq}) \quad (27)$$

Finally, we can wrap up our derivation of the total transition dipole matrix element:

$$\langle \Psi_f | \hat{\mu} | \Psi_i \rangle = \langle \Psi_f^{vib}(\vec{R}) | D^{el}(\vec{R}) | \Psi_i^{vib}(\vec{R}) \rangle \quad (28)$$

$$= \langle \Psi_f^{vib}(\vec{R}) | D^{el}(\vec{R}_{eq}) | \Psi_i^{vib}(\vec{R}) \rangle \quad (29)$$

$$= \langle \Psi_f^{vib}(\vec{R}) | \Psi_i^{vib}(\vec{R}) \rangle D^{el}(\vec{R}_{eq}) \quad (30)$$

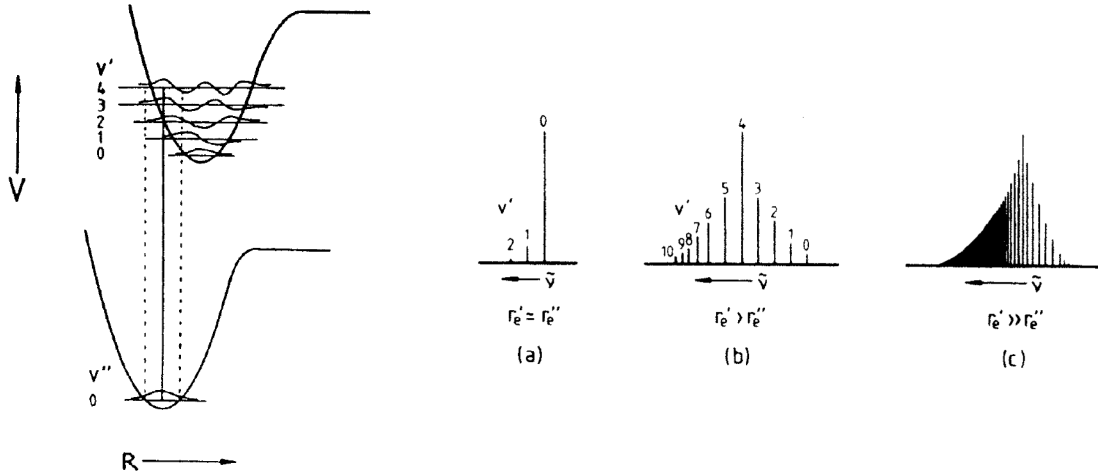
$$= \boxed{\langle \Psi_f^{vib} | \Psi_i^{vib} \rangle \cdot \langle \Psi_f^{el} | \hat{\mu}_e | \Psi_i^{el} \rangle} \quad (31)$$

We've arrived now at the major statement of vibronic selection rules, which has two elements. The intensity of a vibronic transition depends on:

- The electronic transition dipole moment $D^{el}(\vec{R}) = \langle \Psi_f^{el} | \hat{\mu}_e | \Psi_i^{el} \rangle \neq 0$. This quantity tells us whether the transition between two electronic configurations is dipole-allowed. It is most easily evaluated using group theory, where we can take direct product of irreducible representations as a shortcut to evaluating integrals over all space. An electronic transition is dipole-allowed if the direct product $\Gamma_i \otimes \Gamma_{x,y,z} \otimes \Gamma_f$ contains the totally symmetric representation.
- The so-called Franck-Condon factor $\langle \Psi_f^{vib} | \Psi_i^{vib} \rangle$. Note that Ψ_i^{vib} and Ψ_f^{vib} are *not* orthogonal, because they represent eigenfunctions of the vibrational Hamiltonian of two different electronic surfaces. The change in vibrational quantum state that accompanies a change in electronic state depends on the net overlap between the vibrational wavefunction in the initial and final states. The physical interpretation of the Franck-Condon factor is consistent with the original basis of the Born-Oppenheimer principle, namely that nuclei move much more

slowly than electrons. In effect, in the time it takes for an electronic transition to occur, the nuclei do not move. Thus, the band with the highest transition probability is the one for which the transition is “vertical”: the molecule finds itself instantaneously in the excited electronic state with the same internuclear separation as it had in the ground electronic state.

We sketch the FC principle below for a diatomic molecule. Typically the equilibrium bond length in the excited state R'_e is greater than that in the ground state R''_e because electronic excitation tends to weaken bonds. The only regions of the excited state potential that are accessible in the transition are those for which the vibrational wavefunction of the ground state has finite value. In this cartoon the FC factor is largest for the transition $v' = 4 \leftarrow v'' = 0$, though it is also appreciable for neighboring v' . This yields an intensity distribution like that illustrated in panel (b). Such an intensity distribution is called a “vibrational progression,” which involves a series of vibronic transitions between two common electronic states, and with the lower vibrational level in common.



Another useful way to think about the Franck-Condon principle is that upon electronic excitation, we *project* the ground state vibrational wavepacket onto the excited state surface. Let’s sketch very quickly why this is the case. Say we start in the ground vibrational state $|0_g\rangle$ of the electronic ground state $|g\rangle$, and excite to the manifold of $|n_e\rangle$ vibrational states of the electronic excited state $|e\rangle$.

$$|0_g\rangle|g\rangle \xrightarrow{h\nu} |0_g\rangle|g\rangle + \sum_n |n_e\rangle|e\rangle \cdot \langle e|\hat{\mu}_e|g\rangle \cdot \langle n_e|0_g\rangle \quad (32)$$

$$= |0_g\rangle|g\rangle + D^{el} |e\rangle \sum_n |n_e\rangle \cdot \langle n_e|0_g\rangle \quad (33)$$

$$= |0_g\rangle|g\rangle + D^{el} |0_g\rangle|e\rangle \quad (34)$$

where we used the resolution of the identity for a complete set of eigenvectors: $\sum_n |n_e\rangle \cdot \langle n_e| = \hat{I}$.

We can see from this exercise that photoexcitation recreates the *ground state* $|0_g\rangle$ vibrational wavefunction on the excited state surface by populating a series of $|n_e\rangle$ states that form a basis set expansion of $|0_g\rangle$.