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The Born-Oppenheimer approximation

1 Re-writing the Schrödinger equation

We will begin from the full time-independent Schrödinger equation for the eigenstates of a molecular system

$$\left[\sum_n \frac{P_n^2}{2m_n} + \sum_m \frac{P_m^2}{2m_m} + \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{2} \sum_{m,m'} \frac{1}{|\mathbf{r}_m - \mathbf{r}_{m'}|} - \sum_{m,n} \frac{Z_n}{|\mathbf{r}_m - \mathbf{r}_n|} + \frac{1}{2} \sum_{n,n'} \frac{Z_n Z_{n'}}{|\mathbf{r}_n - \mathbf{r}_{n'}|} \right) \right] |\Psi\rangle = E|\Psi\rangle \tag{1}$$

The m index runs over electrons, and n over nuclei. Here I have ignored relativistic corrections to the Hamiltonian $\mathcal{H}$, and assumed that the nuclei are pointlike. The Hamiltonian contains no spin-dependent terms, and so the eigenstates $|\Psi\rangle$ will be factorizable into spin and coordinate parts from now on, I will ignore the spin state and deal with wavefunctions $\Psi(\mathbf{R}; \mathbf{r})\rangle$ where $\mathbf{R}$ and $\mathbf{r}$ are the set of nuclear and electronic positions respectively. This is obviously an insoluble problem without making approximations. To get started, consider the solution of the problem if the nuclei were fixed

$$\left[\sum_m \frac{P_m^2}{2m_m} + \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{2} \sum_{m,m'} \frac{1}{|\mathbf{r}_m - \mathbf{r}_{m'}|} - \sum_{m,n} \frac{Z_n}{|\mathbf{r}_m - \mathbf{R}_n|} + \frac{1}{2} \sum_{n,n'} \frac{Z_n Z_{n'}}{|\mathbf{R}_n - \mathbf{R}_{n'}|} \right) \right] \phi(\mathbf{r}) = E\phi(\mathbf{r}) \tag{2}$$

This Hamiltonian will produce a complete orthogonal set of eigenstates $\phi_s^{\mathbf{R}}(\mathbf{r})$ with energies $E_s(\mathbf{R})$, where s labels the eigenstate and $\mathbf{R}$ reminds us that the eigenstates will be dependent on where we have fixed the nuclear positions.

It is important to see that if $\mathbf{R}$ is changed, the eigenstates $\phi_s^{\mathbf{R}}(\mathbf{r})$ will change continuously, so that eigenstates of the same s at different $\mathbf{R}$ are linked, and form a 'family' of states – see Figure 2. We only run into problems if the families get very close to each other at any point – this is one of the criteria by which the Born-Oppenheimer approximation can break down. Note that for now, we don't actually care about this continuity of families issue, it only arises when we make the adiabatic approximation later. So, as $\phi_s^{\mathbf{R}_a}(\mathbf{r})$ is a complete basis set for electrons if the nuclei are fixed at $\mathbf{R}_a$, any state with such fixed nuclei can be written

$$\Psi_a(\mathbf{R}, \mathbf{r}) = \sum_s c_s \delta(\mathbf{R} - \mathbf{R}_a)\phi_s^{\mathbf{R}_a}(\mathbf{r}). \tag{3}$$

Don't panic about the δ-function: this is just saying that the nuclei are fixed at certain postitions. Now, for our real system in which nuclei can move, a general state will be a sum over all possible $\Psi_a(\mathbf{R}; \mathbf{r})$ with appropriate coeficients (*i.e.*, we take a superposition of all possible locations where the nuclei could be). As $\mathbf{R}_a$ is a continuous variable, our sum becomes an integral

$$\Psi(\mathbf{R}, \mathbf{r}) = \int d\mathbf{R}_a \sum_s c_s(\mathbf{R}_a)\delta(\mathbf{R} - \mathbf{R}_a)\phi_s^{\mathbf{R}_a}(\mathbf{r}). \tag{4}$$
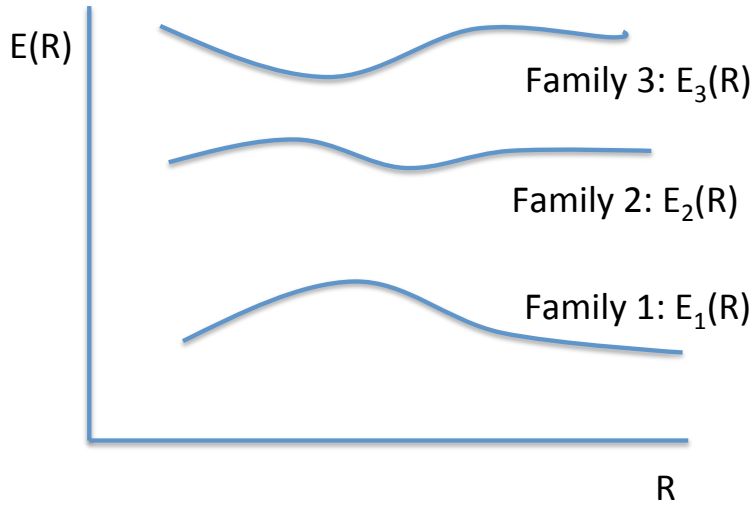
Figure 1: Electron energy eigenvalues as a function of nuclear separation. Note that that they exist in continuous 'families'.

Note that the factor $c_s(\mathbf{R}_a)$ varies with position of the nuclei – this allows the wavefunction to vary with $\mathbf{R}_a$, both in terms of its total magnitude and the relative contributions of different s states. The δ-function does its usual job within the integral, and we are left with

$$\Psi(\mathbf{R}, \mathbf{r}) = \sum_s c_s(\mathbf{R})\phi_s^{\mathbf{R}}(\mathbf{r}) = \sum_s \psi_s(\mathbf{R})\phi_s^{\mathbf{R}}(\mathbf{r}) = \sum_s \phi_s^{\mathbf{R}}(\mathbf{r})\psi_s(\mathbf{R}). \tag{5}$$

So far, we have made no approximations, and I have renamed $c_s(\mathbf{R})$ as $\psi_s(\mathbf{R})$ as we now have something that looks like a wavefunction for the nuclei. The next step is to substitute Equation 5 into Equation 1, giving

$$\mathcal{H}\left(\sum_s \phi_s^{\mathbf{R}}(\mathbf{r})\psi_s(\mathbf{R})\right) = \sum_s \sum_n \frac{P_n^2}{2m_n}\phi_s^{\mathbf{R}}(\mathbf{r})\psi_s(\mathbf{R})$$

$$+\sum_s \left[\sum_m \frac{P_m^2}{2m_m} + \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{2}\sum_{m,m'}\frac{1}{|\mathbf{r}_m-\mathbf{r}_{m'}|} - \sum_{m,n}\frac{Z_n}{|\mathbf{r}_m-\mathbf{R}_n|} + \frac{1}{2}\sum_{n,n'}\frac{Z_n Z_{n'}}{|\mathbf{R}_n-\mathbf{R}_{n'}|}\right)\right]\phi_s^{\mathbf{R}}(\mathbf{r})\psi_s(\mathbf{R})$$

$$= E\sum_s \phi_s^{\mathbf{R}}(\mathbf{r})\psi_s(\mathbf{R}). \tag{6}$$

I have simply split the Hamiltonian into two and swapped the order of summations. Helpfully, we know that $\phi_s^{\mathbf{R}}(\mathbf{r})$ are eigenstates of the second part of the Hamiltonian, so

$$\sum_s \sum_n \frac{P_n^2}{2m_n}\phi_s^{\mathbf{R}}(\mathbf{r})\psi_s(\mathbf{R}) + \sum_s E_s(\mathbf{R})\phi_s^{\mathbf{R}}(\mathbf{r})\psi_s(\mathbf{R}) = E\sum_s \phi_s^{\mathbf{R}}(\mathbf{r})\psi_s(\mathbf{R}). \tag{7}$$

But where do we go from here? It would be nice to get rid of the $\phi_s^{\mathbf{R}}(\mathbf{r})$ – we can try to do this by multiplying by $\phi_s^{*\mathbf{R}}(\mathbf{r})$ and integrating through with respect to $\mathbf{r}$, as we know that the different $\phi_s^{\mathbf{R}}(\mathbf{r})$ are orthogonal at given $\mathbf{R}$. Mathematically, this can be expressed as

$$\int d\mathbf{r}\, \phi_{s'}^{*\mathbf{R}}(\mathbf{r})\phi_s^{\mathbf{R}}(\mathbf{r}) = \delta_{s,s'}. \tag{8}$$

When we do this, the summation and $\phi_s^{\mathbf{R}}(\mathbf{r})$ are indeed eliminated from the second two terms of Equation 7. Unfortunately the first remains difficult, particularly as P_n is a differential

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operator. Therefore

$$\sum_s \left[\int \mathrm{d}\mathbf{r}\, \phi_{s'}^{*\mathbf{R}}(\mathbf{r}) \left(\sum_n \frac{P_n^2}{2m_n} \right) \phi_s^{\mathbf{R}}(\mathbf{r}) + E_s(\mathbf{R})\delta_{s,s'} \right] \psi_s(\mathbf{R}) = E\psi_{s'}(\mathbf{R}). \tag{9}$$

2 The adiabatic approximation

Now comes our first approximation. We would like the sum in Equation 9 to disappear – if you remember, this sum comes from the sum in Equation 5. Could we justify getting rid of the sum here? In general, the nuclei are far more massive than the electrons, and hence will move comparatively slowly. We make the approximation that the nuclei move so slowly that the electrons respond 'adiabatically'.
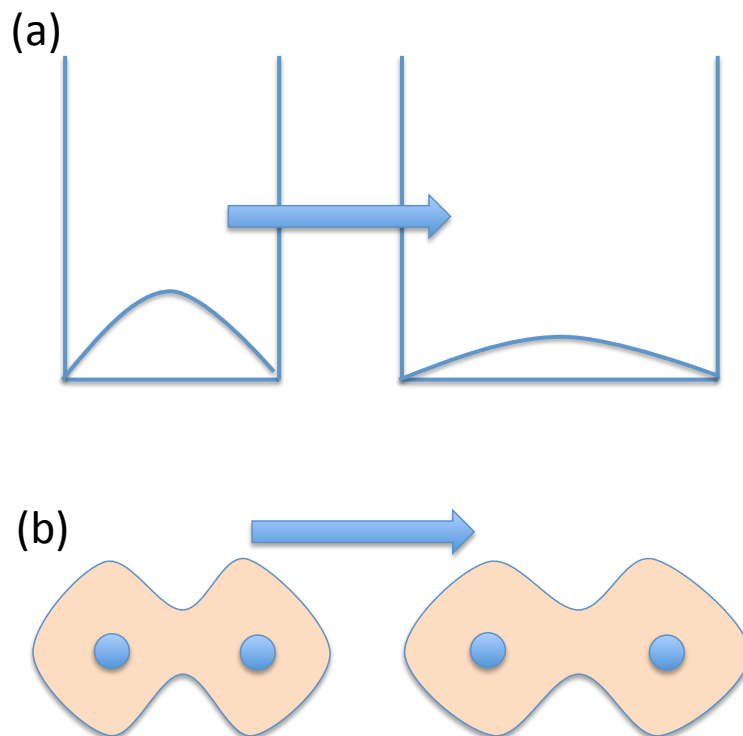
Figure 2: Adiabatic approximation for (a) a particle in a well and (b) electrons in a diatomic molecule. If the walls/nuclei move slowly enough, the particle / electrons will remain in a given continuously connected family of states. In other words, at the end of the process they will be in a state of the new system which corresponds to the state of the old system in which they started.

Remember the particle in a box from elementary QM. Now imagine changing the location of the walls – if we do this slowly enough, it seems reasonable enough to assume that a particle in the groundstate of the system will continuously evolve into the new groundstate. Of course it's energy will not be constant – in fact, it is doing work on whatever is moving the walls in place. But the point is that it moves between continuously connected groundstates. The Wikipedia page for 'Adiabatic theorem' is quite good, if you want more details. The argument also holds for any state, provided that energy levels do not get too close and that the change in Hamiltonian is slow enough.

How is this relevant to us? Let us step back, and view the nuclei as an external potential acting on the electrons. We already have a set of electronic eigenstates $\phi_s^{\mathbf{R}}(\mathbf{r})$ for any configuration of nuclei. By making the adiabatic approximation, we are saying that the nuclei move slowly enough that the electrons will not change which family of states they are in when this movement occurs (*i.e.*, the s index does not change). This is shown graphically in Figure 2. Or, mathematically, if the nuclei move from $\mathbf{R} \to \mathbf{R}'$, electrons in an eigenstate will change as

$$\phi_s^{\mathbf{R}}(\mathbf{r}) \to \phi_s^{\mathbf{R}'}(\mathbf{r}) \tag{10}$$

Now, what does this mean when we want to consider the nuclei as part of the system, rather than an external potential? Let us imagine we start in a state which contains contributions from only one s-state family, which we shall call $s = 0$

$$\Psi(\mathbf{R}, \mathbf{r}) = \psi(\mathbf{R})\phi_s^{\mathbf{R}}(r) \tag{11}$$

What happens as time progresses? This is not necessarily an eigenstate of the whole system, and so the state will tend to change. However, having made the adiabatic approximation, we know that allowing the nuclei to move will not cause the electrons to change which s-family they are in! So we know that the Hamiltonian does not connect different s-families, and therefore that eigenstates will be confined to one s-family. In other words, we can write that a general eigenstate of the system is necessarily given by

$$\Psi_{s,t}^E(\mathbf{R}, \mathbf{r}) = \psi_{s,t}(\mathbf{R})\phi_s^{\mathbf{R}}(r) \tag{12}$$

Here, s and t label the particular eigenstate – we have the tth eigenstate of the s-family of electron states. So we have got rid of our sum, which is what we wanted. Now Equation 9 becomes

$$\left[\int \mathrm{d}\mathbf{r}\, \phi_s^{*\mathbf{R}}(\mathbf{r}) \left(\sum_n \frac{P_n^2}{2m_n}\right) \phi_s^{\mathbf{R}}(\mathbf{r}) + E_s(\mathbf{R})\right] \psi_{s,t}(\mathbf{R}) = E_{s,t}\psi_{s,t}(\mathbf{R}). \tag{13}$$

3 Fully simplifying the equation for diatomic molecules

The first term is still a bit annoying – it contains a differential operator on nuclear positions, which is acting on both $\phi_s^{\mathbf{R}}(\mathbf{r})$ and $\psi_{s,t}(\mathbf{R})$. It would be nice to be able to assume that $\nabla_{\mathbf{R}}\phi_s^{\mathbf{R}}(\mathbf{r}) = 0$ so that we could take the differential operator out of the integral (which would then simply be unity), leaving

$$\left[\left(\sum_n \frac{P_n^2}{2m_n}\right) + E_s(\mathbf{R})\right] \psi_{s,t}(\mathbf{R}) = E_{s,t}\psi_{s,t}(\mathbf{R}), \tag{14}$$

which looks like a Schrödinger equation for nuclei, with a potential dependent on electronic configurations.

For a diatomic molecule, we can describe the two nuclei using only a relative coordinate in the reduced mass formalism (here we are assuming that the centre of mass frame is the centre of mass frame of the nuclei - reasonable, given how light the electrons are). The centre of mass evolution is then separable and trivial, and I shall ignore it. In this case, Equation 13 reduces to

$$\left[\int \mathrm{d}\mathbf{r}\, \phi_s^{*\mathbf{R}}(\mathbf{r}) \left(\frac{-\hbar^2 \nabla_{\mathbf{R}}^2}{2\mu}\right) \phi_s^{\mathbf{R}}(\mathbf{r}) + E_s(\mathbf{R})\right] \psi_{s,t}(\mathbf{R}) = E_{s,t}\psi_{s,t}(\mathbf{R}), \tag{15}$$

with $\mathbf{R}$ now representing the relative coordinate of the nuclei, and μ the reduced mass. Note that the electronic energy an only depend on the separation of nuclei in the diatomic case. We can also split the differential operator into radial and angular parts

$$\frac{-\hbar^2 \nabla_{\mathbf{R}}^2}{2\mu} = \frac{-\hbar^2 \nabla_R^2}{2\mu} + \frac{\mathbf{L}_{\mathbf{R}}^2}{2\mu R^2}, \tag{16}$$

where $\mathbf{L}_{\mathbf{R}}$ is the orbital angular momentum of the nuclei. Physically, we know that the distance between nuclei in a molecule varies very little, and so the nuclear part of the wavefunction will be very strongly peaked around some $|\mathbf{R}|$. By contrast, the electronic state $\phi_s^{\mathbf{R}}(\mathbf{r})$ will be relatively insensitive to $|\mathbf{R}|$ in this region: the electron orbitals will care very little about these small changes in nuclear separation. So it seems reasonable that the radial component of the differential operator would essentially only act on $\psi_{s,t}(\mathbf{R})$.

What about the angular part? We can't say that the nuclear wavefunction is strongly peaked around one direction of $\mathbf{R}$. However, let us consider the total orbital angular momentum of the system, $\mathbf{K} = \mathbf{L}_{\mathbf{R}} + \mathbf{L}_{\mathbf{r}}$ (with $\mathbf{L}_{\mathbf{r}}$ being the orbital angular momentum of the electrons). Then

$$\mathbf{L}_{\mathbf{R}}^2 = \mathbf{K}^2 - 2\mathbf{L}_{\mathbf{r}}.\mathbf{L}_{\mathbf{R}} - \mathbf{L}_{\mathbf{r}}^2. \tag{17}$$

We can substitute this expression into Equation 16, and then into Equation 15. First of all, we note that $\mathbf{K}^2$ is a conserved quantity of the system because there is no external torque and so we can choose are eigenstates such that

$$\mathbf{K}^2 \phi_s^{\mathbf{R}}(\mathbf{r})\psi_{s,t}(\mathbf{R}) = \hbar^2 K(K+1)\phi_s^{\mathbf{R}}(\mathbf{r})\psi_{s,t}(\mathbf{R}) \tag{18}$$

where K is the angular momentum quantum number of the state in question. What about

$$\left[\int d\mathbf{r}\, \phi_s^{*\mathbf{R}}(\mathbf{r}) \left(\mathbf{L}_{\mathbf{r}}.\mathbf{L}_{\mathbf{R}} \right) \phi_s^{\mathbf{R}}(\mathbf{r}) \right] \psi_{s,t}(\mathbf{R})? \tag{19}$$

To treat this, we note that only the component of $\mathbf{L}_{\mathbf{r}}$ along the internuclear axis $\mathbf{R}$ is a conserved quantity, because the potential experienced by electrons is only symmetric about the $\mathbf{R}$ axis. However, the angular momentum of the nuclei is *necessarily zero* along this internuclear axis (the nuclei have zero moment of inertia about this axis). We can then make an argument analogous to the vector model in atomic physics to claim that the whole expression is zero. What about the final term

$$\left[\int d\mathbf{r}\, \phi_s^{*\mathbf{R}}(\mathbf{r}) \left(\mathbf{L}_{\mathbf{r}}^2 \right) \phi_s^{\mathbf{R}}(\mathbf{r}) \right] \psi_{s,t}(\mathbf{R})? \tag{20}$$

We cannot argue that this is zero. However, the part within square brackets is not a differential operator. In fact, it is simply a function of R and s (the expectation of $\mathbf{L}_{\mathbf{r}}^2$ for a given s should not depend on the internuclear orientation, just like $E_s(R)$). Therefore this term can simply be swallowed into a slightly modified $E_s(R)$, $E_s'(R)$.

Our equation for $\psi_{s,t}(\mathbf{R})$ has substantially simplified to

$$\left[\frac{-\hbar^2 \nabla_R^2}{2\mu} + \frac{K(K+1)\hbar^2}{2\mu R^2} + E_s'(R) \right] \psi_{s,t}(\mathbf{R}) = E_{s,t}\psi_{s,t}(\mathbf{R}). \tag{21}$$

The operator on the LHS of the above equation is purely radial. We can therefore split up the radial and angular parts of the wavefunction, $\psi_{s,t}(\mathbf{R}) = \rho_{s,t}(R)\Omega_{s,t}(\Theta, \Phi)$. The radial part obeys

$$\left[\frac{-\hbar^2 \nabla_R^2}{2\mu} + \frac{K(K+1)\hbar^2}{2\mu R^2} + E_s'(R) \right] \rho_{s,t}(R) = E_{s,t}\rho_{s,t}(R), \tag{22}$$

and the angular part is such that Equation 18 is obeyed, which was assumed when we wrote down Equation 21. Note that $\Omega_{s,t}(\Theta, \Phi)$ is *not* an eigenstate of nuclear angular momentum, which is not a conserved quantity.

4 The end result

Thus we have arrived at the much simpler (and physically meaningful) equations of the Born-Oppenheimer approximation. We first solve for the electronic eigenstates $\phi_s^{\mathbf{R}}(\mathbf{r})$ fixed nuclear positions (Equation 2), and then use the eigenvalues to find nuclear eigenstates $\psi_{s,t}(\mathbf{R})$ (Equations 18 and 22). Having found $\phi_s^{\mathbf{R}}(\mathbf{r})$ and $\psi_{s,t}(\mathbf{R})$, our overall eigenstates are simply

$$\Psi_{s,t}^E(\mathbf{R}, \mathbf{r}) = \psi_{s,t}(\mathbf{R})\phi_s^{\mathbf{R}}(r) \tag{23}$$

At this stage, our approximations are the adiabatic assumption, and that the nuclear wavefunction depends much more strongly on $|\mathbf{R}|$ than the electronic configuration. To go further, we assume that the potential well $E_s'(R)$ is approximately quadratic about $R = R_s$, and that deviations from R_s are small, giving us our energy spectrum

$$E_{s,t} \approx E_s'(R_s) + \frac{K_{t,s}(K_{t,s} + 1)\hbar^2}{2\mu R_s^2} + \hbar\omega_s\left(\nu_t + \frac{1}{2}\right) \tag{24}$$

The s and t labels indicate quantities that depend on which electronic configuration and nuclear wavefunction you are in, respectively. They can be left out if this distinction is not required. It is important to remember that the K quantum number is for the total orbital angular momentum of the molecule, not just the nuclei. In practice, when analysing energy levels, this is often not that important. However, because the nuclei cannot have angular momentum along the vector between them, the component of electronic angular momentum along this axis (quantum number Λ) is particularly important. If $\Lambda > 0$, then it is *impossible* to have $K = 0$ because we know that there is angular momentum along this axis. In fact, you should be able to convince yourself that $K \geq \Lambda$. Therefore the permissible values of K are limited by the electronic state $\phi_s^{\mathbf{R}}(\mathbf{r})$.

5 Electric dipole transitions in diatomic molecules

We are interested in the electric dipole matrix element

$$|M_{21}|^2 = \mathrm{e}^2|\langle\Psi_2|\left(\sum_n Z_n\mathbf{R}_n - \sum_m \mathbf{r_m}\right).\mathbf{E}\,|\Psi_1\rangle|^2 = \mathrm{e}^2|\langle\Psi_2|\,\mathbf{D}.\mathbf{E}\,|\Psi_1\rangle|^2. \tag{25}$$

Substituting in using Equation 12, we have

$$M_{21} = \mathrm{e}\int\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{R}\,\psi_{s_2,t_2}^*(\mathbf{R})\phi_{s_2}^{*\mathbf{R}}(\mathbf{r})\,(\mathbf{D}.\mathbf{E})\,\psi_{s_1,t_1}(\mathbf{R})\phi_{s_1}^{\mathbf{R}}(\mathbf{r})$$

$$= \mathrm{e}\int \mathrm{d}\mathbf{R}\,\left[\int \mathrm{d}\mathbf{r}\,\phi_{s_2}^{*\mathbf{R}}(\mathbf{r})\mathbf{D}\phi_{s_1}^{\mathbf{R}}(\mathbf{r})\right].\mathbf{E}\,\psi_{s_2,t_2}^*(\mathbf{R})\psi_{s_1,t_1}(\mathbf{R}) \tag{26}$$

$$= \mathrm{e}\int \mathrm{d}\mathbf{R}\,(\mathbf{d}_{21}(\mathbf{R}).\mathbf{E})\,\psi_{s_2,t_2}^*(\mathbf{R})\psi_{s_1,t_1}(\mathbf{R}).$$

The above equation defines the useful quantity $\mathbf{d}_{21}(\mathbf{R})$. How will this quantity depend on $\mathbf{R}$? Firstly, as we did in deriving the energy levels, we could assume that electron states are less sensitive to $|\mathbf{R}|$ than the the nuclear wavefunctions, because the nuclei are assumed to vibrate only a little. Thus $\mathbf{d}_{21}(\mathbf{R}) \approx \mathbf{d}_{21}(\Theta, \Phi)$ and we can write

$$M_{21} = \mathrm{e}\left(\int \mathrm{d}R\,R^2\rho_{s_2,t_2}^*(R)\rho_{s_1,t_1}(R)\right)\left(\int \mathrm{d}\Theta\mathrm{d}\Phi\,\sin\Theta\,(\mathbf{d}_{21}(\Theta,\Phi).\mathbf{E})\,\Omega_{s_2,t_2}^*(\mathbf{R})\Omega_{s_1,t_1}(\mathbf{R})\right), \tag{27}$$

where I have used the splitting $\psi_{s,t}(\mathbf{R}) = \rho_{s,t}(R)\Omega_{s,t}(\Theta, \Phi)$ introduced when the nuclear equation was discussed. Why bother to do this?

- The first factor in Equation 27 is the Frank-Condon factor, which tells us that when we transitions between different electronic configurations, the strength depends on the overlap of the vibrational wavefunctions.

- Our result therefore seems to forbid ro-vibrational transitions if the electronic state does not change. However, the simplification that $\mathbf{d}_{21}$ is R-independent is not quite true. As a result, we do get ro-vibrational changes within the same electronic configuration, with ± 1 being the most likely.

It is also worth noting that homonuclear diatomic molecules cannot have transitions involving no change of electronic state. When the nuclei are identical, $\sum_n Z_n \mathbf{R}_n = 0$ and hence the dipole operator $\mathbf{D}$ has no $\mathbf{R}$ dependence. It is then simply an odd function of the electronic coordinates. If the electronic state does not change, $\mathbf{d}_{21}$ is then an integral of an odd function (as the electronic states have definite parity in a homonuclear molecule) and necessarily zero.

Further selection rules can be obtained through considering the conservation of angular momentum.