

## 23 The Born-Oppenheimer approximation, the Many Electron Hamiltonian and the molecular Schrödinger Equation

1. Now we will write down the Hamiltonian for a molecular system comprising  $N$  nuclei and  $n$  electrons. In general this Hamiltonian will contain the following terms (note we are using lower case for electrons upper case for nuclei):

(a) The nuclear kinetic energy term.

$$-\frac{\hbar^2}{2} \sum_{I=1}^N \frac{1}{M_I} \nabla_I^2 \quad (23.1)$$

(b) The electronic kinetic energy term.

$$-\frac{\hbar^2}{2m} \sum_{i=1}^n \nabla_i^2 \quad (23.2)$$

(c) The electron-nuclear attraction.

$$-\sum_{I=1}^N \sum_{i=1}^n \frac{Ze^2}{r_{i,I}} \quad (23.3)$$

(d) The nuclear-nuclear repulsion.

$$+\sum_{I=1}^N \sum_{J=1}^{N'} \left[ \frac{Z_I Z_J e^2}{r_{I,J}} \right] \quad (23.4)$$

The summation here is restricted so there is no double counting (that is you should not have the  $(I, J)$  and  $(J, I)$  terms) and that  $I \neq J$ . Finally,

(e) The electron-electron repulsion.

$$+ \sum_{i=1}^n \sum_{j=1}^{n'} \left[ \frac{e^2}{r_{i,j}} \right] \quad (23.5)$$

Here again the summation is restricted so there no double counting (that is you should not have the  $(i, j)$  and  $(j, i)$  terms) and that  $i \neq j$ . This last innocuous looking term is actually a major challenge. All quantum chemistry methods are ways to approximate this term. The exact solution for anything more than 1 electron is unknown!! Some approaches that effectively approximate this term for a number of systems include, density functional theory (very powerful and applicable for large systems), coupled cluster (very expensive, but very accurate), configuration interaction (rigorous but not used due to some major defects). There are others which will be discussed in the next course.

2. So the total molecular Hamiltonian is just the sum of these different terms:

$$H = -\frac{\hbar^2}{2} \sum_{I=1}^N \frac{1}{M_I} \nabla_I^2 - \frac{\hbar^2}{2m} \sum_{i=1}^n \nabla_i^2 - \sum_{I=1}^N \sum_{i=1}^n \frac{Z_I e^2}{r_{i,I}} + \sum_{I=1}^N \sum_{J=1}^{N'} \left[ \frac{Z_I Z_J e^2}{r_{I,J}} \right] + \sum_{i=1}^n \sum_{j=1}^{n'} \left[ \frac{e^2}{r_{i,j}} \right] \quad (23.6)$$

3. The time-independent Schrödinger Equation obtained from substituting the Hamiltonian in Eq. (23.6) is actually impossible to solve exactly and approximations are required. One powerful approximation is called the Born-Oppenheimer approximation. (It does have some limitations and we will discuss these as well.) The Born-Oppenheimer approximation assumes that the nuclei are infinitely heavy as compared to the electrons. Hence the nuclei can be assumed to be stationary objects while the electrons go about doing whatever it is that they do. Mathematically what this does for us is, it allows us to write the full wavefunction (a function of the electronic positions  $r_i$  and nuclear positions  $R_I$ ) in *separable form*:

$$\Psi(r_i, R_I) = \phi(r_i, \{R_I\})\chi(R_I) \quad (23.7)$$

where  $\phi(r_i, \{R_I\})$  is an electronic wavefunction that parametrically depends on the nuclear positions (what is meant by this we will see in a little while), and  $\chi(R_I)$  is the nuclear wavefunction. The function  $\phi(r_i, \{R_I\})$  represents the electronic states for fixed nuclear configurations  $\{R_I\}$ . (That is the nuclei are frozen and then the appropriate electronic structure is  $\phi(r_i, \{R_I\})$ . As we stated earlier this is a result of the infinite mass of the nuclei with respect to electrons.)  $\chi(R_I)$ , the nuclear wavefunction, is actually the solution to the ro-vibrational problem for the nuclear coordinates in the presence of an electronic potential energy surface. (We will see more on this in a little while as well!!)

4. Caveat: Eq. (23.7) is not completely general. It fails in many known situations. One example is when ground and excited electronic surfaces get very close. (This happens more often in molecular systems than you would imagine.) These cases have to be treated differently and more carefully, and these fall into the domain of what is known as non-adiabatic quantum dynamics (as opposed to Born-Oppenheimer approximation being considered the adiabatic approximation).
5. Having got over that caveat we will proceed further with the analysis of Eq. (23.7) since it is useful in many cases and in most cases it is the only thing we can do, at the present time. So, Eq. (23.7) is a product form, and by now we know well how to handle such product forms in the time-independent Schrödinger Equation. *We perform the separation of variables, apply the Born-Oppenheimer approximation (that is assume the nuclei are infinitely heavy as compared to the electrons) and end up with two different Schrödinger Equations, one for the nuclei and one for the electrons.* For the electrons we have

$$\left[ -\frac{\hbar^2}{2m} \sum_{i=1}^n \nabla_i^2 - \sum_{I=1}^N \sum_{i=1}^n \frac{Ze^2}{r_{i,I}} + \sum_{I,J=1}^N \frac{Z_I Z_J e^2}{r_{I,J}} + \sum_{i,j=1}^n \frac{e^2}{r_{i,j}} \right] \phi(r_i, \{R_I\}) = U_n(\{R_I\}) \phi(r_i, \{R_I\}) \quad (23.8)$$

The nuclei are assumed to be fixed in this equation. That is the nuclear coordinates  $\{R_I\}$  are fixed within some conformation of the molecule.  $U_n(\{R_I\})$  is called the electronic energy. Note it is a function of the nuclear coordinates  $\{R_I\}$  we chose. So this gives us a potential energy surface that the nuclei feel. This potential energy surface enters into the nuclear Schrödinger Equation:

$$\left[ -\frac{\hbar^2}{2} \sum_{I=1}^N \frac{1}{M_I} \nabla_I^2 + U_n(\{R_I\}) \right] \chi(R_I) = E\chi(R_I) \quad (23.9)$$

As stated earlier the function  $\chi(R_I)$  contains all the information you need about rotations and vibrations including coupling between them (provided they are not decoupled when you solve Eq. (23.9)). In fact you can also chemical reaction dynamics using Eq. (23.9) *provided you know  $U_n(\{R_I\})$  for every single nuclear geometry there is to know!!* It is obviously not possible to know the value of  $U_n(\{R_I\})$  for *every single nuclear geometry* since that would entail the solution to Eq. (23.8) for every single geometry (which is hard for one geometry let alone every single one). So, generally what is done is a large number of  $U_n(\{R_I\})$  by solving Eq. (23.8) for a finite number of nuclear geometries and these energies are fitted using some function and the resultant function is used in Eq. (23.9) which is then solved for a chemical reaction or for ro-vibrational states.

6. This back and forth solution between Eqs. (23.8) and (23.9) is clearly not easy and clearly not possible for every single required structure, and that is the reason *ab initio* molecular dynamics has been developed recently to simultaneously *solve* the electronic and nuclear problem for both reaction dynamics and for ro-vibrational states.
7. Here the approach called Born-Oppenheimer dynamics is something that becomes relevant. What happens here is Eq. (23.8) for a given nuclear geometry to obtain  $U_n(\{R_I\})$ . Then the derivative of this energy with respect to the nuclear degrees of freedom,  $\frac{\partial U_n(\{R_I\})}{\partial R_I}$  is calculated. (This is a very expensive calculation!!) Note now, this partial derivative is the classical definition of the force on the nuclei. (Force is gradient of energy with respect to coordinates in classical mechanics.) Then the force  $\frac{\partial U_n(\{R_I\})}{\partial R_I}$  is used to move the nuclei on an  $F = ma$  type approach. (That is the nuclei are classical in Born-Oppenheimer dynamics unlike in Eq. (23.9) where these are quantum-mechanical.)
8. A little bit explanation on Born-Oppenheimer dynamics and non-adiabatic dynamics.

9. We have discussed how the full time-independent Schrödinger Equation for electrons and nuclei can be reduced so as to solve the nuclear and electronic problems independently. This was done based on the large separation between the nuclear and electronic masses and hence the inferred large separation in their momenta and was known as the Born-Oppenheimer approximation.
10. This approximation lead us to the Eqs. (23.8) and (23.9), the solutions to which would provide us with the independent electronic states and the nuclear states. (Note these are both still eigenvalue problems.)
11. We also noted that in some cases the Born-Oppenheimer approximation breaks down. And in such cases a separable form for the full wavefunction as in Eq. (23.7) cannot be enforced. These happen for example when ground and excited electronic surfaces get very close. Such cases fall under the regime of non-adiabatic quantum dynamics. We talked about how a simple product like Eq. (23.7) is no longer valid in such cases and in fact a sum of such products is necessary. This leads to coupled equations involving both the electrons and the nuclei. Some of the terms that you get out of such a treatment are called the non-adiabatic coupling elements.
12. The Born-Oppenheimer approximation Eqs. (23.8) and (23.9) are of course much simpler (they certainly look simpler although even Eqs. (23.8) and (23.9) are not really simple for most cases in chemistry).

13. We also briefly hinted on time-dependent methodologies. One of which is rather interesting and essentially leads to classical,  $F = ma$ , type equations for the nuclei and Eq. (23.8) for the electrons. This set of equations together characterize what is known as *Born-Oppenheimer dynamics*. (Note this is different from Born-Oppenheimer separation above which is *time-independent*.)
14. So we have actually very briefly discussed a whole myriad of approaches to treat the electron-nuclear problem. These are all actually hot topics of research today. We will now move on to look at Eq. (23.8) more carefully.