G25.2666: Quantum Chemistry and Dynamics

Notes for Lecture 10

I. THE BORN-OPPENHEIMER APPROXIMATION

The next few lectures will treat the problem of quantum chemistry, a subfield of quantum mechanics also known as molecular quantum mechanics. The idea of quantum chemistry is to use only the simple facts molecules and, indeed, all of ordinary matter, can be viewed as composed only of positively charged nuclei and negatively charged electrons. This *universal* description is then subject to a quantum mechanical treatment from which the properties of the system are derived or computed.

We begin our discussion of AIMD by considering a system of N nuclei described by coordinates, $\mathbf{R}_1, ..., \mathbf{R}_N \equiv \mathbf{R}$, momenta, $\mathbf{P}_1, ..., \mathbf{P}_N \equiv \mathbf{P}$, and masses $M_1, ..., M_N$, and N_e electrons described by coordinates, $\mathbf{r}_1, ..., \mathbf{r}_{N_e} \equiv \mathbf{r}$, momenta, $\mathbf{p}_1, ..., \mathbf{p}_{N_e} \equiv \mathbf{p}$, and spin variables, $s_1, ..., s_{N_e} \equiv s$. The Hamiltonian of the system is given by

$$H = \sum_{I=1}^{N} \frac{\mathbf{P}_I^2}{2M_I} + \sum_{i=1}^{N_e} \frac{\mathbf{p}_i^2}{2m} + \sum_{i>j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{I>J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} - \sum_{i,I} \frac{Z_I e^2}{|\mathbf{R}_I - \mathbf{r}_i|}$$

$$\equiv T_{\mathrm{N}} + T_{\mathrm{e}} + V_{\mathrm{ee}}(\mathbf{r}) + V_{\mathrm{NN}}(\mathbf{R}) + V_{\mathrm{eN}}(\mathbf{r}, \mathbf{R})$$

where m is the mass of the electron, and $Z_I e$ is the charge on the Ith nucleus. In the second line, T_{N}, T_{e}, V_{ee}, V_{NN}, and V_{eN} represent the nuclear and electron kinetic energy operators and electron-electron, electron-nuclear, and nuclear-nuclear interaction potential operators, respectively. Note that this Hamiltonian is universal in that it describes all of everyday matter from biological macromolecules such as proteins, enzymes and nucleic acids, to metals and semiconductors to synthetic materials such as plastics. Thus, if we could solve for the eigenvalues and eigenfunctions of this Hamiltonian, we could, predict any property we wished of a given system. This fact lead the physicist P. A. M. Dirac to comment that all of chemistry is a solved problem, at least, in principle. Of course, the problem cannot actually be solved exactly, so approximation methods are needed and it is in the development of approximation methods and an analysis of their accuracy that quantum chemistry is focused.

If we sought to solve the complete quantum mechanical problem, we start by seeking the eigenfunctions and eigenvalues of this Hamiltonian, which will be given by solution of the time-independent Schrödinger equation

$$\left[T_{\mathrm{N}} + T_{\mathrm{e}} + V_{\mathrm{ee}}(\mathbf{r}) + V_{\mathrm{NN}}(\mathbf{R}) + V_{\mathrm{eN}}(\mathbf{r}, \mathbf{R}) \right] \Psi(\mathbf{x}, \mathbf{R}) = E\Psi(\mathbf{x}, \mathbf{R}) \tag{1}$$

where $\mathbf{x} \equiv (\mathbf{r}, s)$ denotes the full collection of electron position and spin variables, and $\Psi(\mathbf{x}, \mathbf{R})$ is an eigenfunction of H with eigenvalue E. Clearly, an exact solution of Eq. (1) is not possible and approximations must be made. We first invoke the Born-Oppenheimer approximation by recognizing that, in a dynamical sense, there is a strong separation of time scales between the electronic and nuclear motion, since the electrons are lighter than the nuclei by three orders of magnitude. In terms of Eq. (1), this can be exploited by assuming a quasi-separable ansatz of the form

$$\Psi(\mathbf{x}, \mathbf{R}) = \phi(\mathbf{x}, \mathbf{R})\chi(\mathbf{R}) \tag{2}$$

where $\chi(\mathbf{R})$ is a nuclear wave function and $\phi(\mathbf{x}, \mathbf{R})$ is an electronic wave function that depends parametrically on the nuclear positions.

The Born-Oppenheimer (named for its original inventors, Max Born and Robert Oppenheimer) is based on the fact that nuclei are several thousand times heavier than electrons. The proton, itself, is approximately 2000 times more massive than an electron. In a dynamical sense, the electrons can be regarded as particles that follow the nuclear motion adiabatically, meaning that they are "dragged" along with the nuclei without requiring a finite relaxation time. This, of course, is an approximation, since there could be non-adiabatic effects that do not allow the electrons to follow in this "instantaneous" manner, however, in many systems, the adiabatic separation between electrons and nuclei is an excellent approximation. Another consequence of the mass difference between electrons and nuclei is that the nuclear components of the wave function are spatially more localized than the electronic component of the wave function. In the classical limit, the nuclear are fully localized about single points representing classical point particles. Thus, it follows that the nuclear wave function rises more steeply than the electronic wave function, which means that $\nabla_I \chi(\mathbf{r}) \gg \nabla_I \phi(\mathbf{x}, \mathbf{R})$, from which we may approximate

$$T_{\mathrm{N}} \tag{3}$$

$$psi(\mathbf{x}, \mathbf{r})\chi(\mathbf{R}) = -\frac{\hbar^2}{2}\sum_{I=1}^{N}\frac{1}{M_I}\left[\psi(\mathbf{x}, \mathbf{R})\nabla_I^2\chi(\mathbf{R}) + \chi(\mathbf{R})\nabla_I^2\psi(\mathbf{x}, \mathbf{R}) + 2\nabla_I\psi(\mathbf{x}, \mathbf{R})\cdot\nabla_I\phi(\mathbf{x}, \mathbf{R})\right]$$

$$\approx -\frac{\hbar^2}{2}\sum_{I=1}^{N}\frac{1}{M_I}\psi(\mathbf{x}, \mathbf{R})\nabla_I^2\chi(\mathbf{R}) \tag{4}$$

Substitution of Eq. (2) into Eq. (1) and using the approximation that the nuclear wave function $\chi(\mathbf{R})$ is more localized than the electronic wave function, i.e. $\nabla_I\chi(\mathbf{R}) \gg \nabla_I\phi(\mathbf{x}, \mathbf{R})$, yields

$$\frac{[T_{\mathrm{e}} + V_{\mathrm{ee}}(\mathbf{r}) + V_{\mathrm{eN}}(\mathbf{r}, \mathbf{R})]\,\phi(\mathbf{x}, \mathbf{R})}{\phi(\mathbf{x}, \mathbf{R})} = E - \frac{[T_{\mathrm{N}} + V_{\mathrm{NN}}(\mathbf{R})]\,\chi(\mathbf{R})}{\chi(\mathbf{R})} \tag{5}$$

From the above, it is clear that the left side can only be a function of $\mathbf{R}$ alone. Let this function be denoted, $\varepsilon(\mathbf{R})$. Thus,

$$\frac{[T_{\mathrm{e}} + V_{\mathrm{ee}}(\mathbf{r}) + V_{\mathrm{eN}}(\mathbf{r}, \mathbf{R})]\,\phi(\mathbf{x}, \mathbf{R})}{\phi(\mathbf{x}, \mathbf{R})} = \varepsilon(\mathbf{R})$$

$$[T_{\mathrm{e}} + V_{\mathrm{ee}}(\mathbf{r}) + V_{\mathrm{eN}}(\mathbf{r}, \mathbf{R})]\,\phi(\mathbf{x}, \mathbf{R}) = \varepsilon(\mathbf{R})\phi(\mathbf{x}, \mathbf{R}) \tag{6}$$

Eq. (6) is an electronic eigenvalue equation for an electronic Hamiltonian, $H_{\mathrm{e}}(\mathbf{R}) = T_{\mathrm{e}} + V_{\mathrm{ee}}(\mathbf{r}) + V_{\mathrm{eN}}(\mathbf{r}, \mathbf{R})$ which will yield a set of normalized eigenfunctions, $\phi_n(\mathbf{x}, \mathbf{R})$ and eigenvalues, $\varepsilon_n(\mathbf{R})$, which depend parametrically on the nuclear positions, $\mathbf{R}$. For each solution, there will be a nuclear eigenvalue equation:

$$[T_{\mathrm{N}} + V_{\mathrm{NN}}(\mathbf{R}) + \varepsilon_n(\mathbf{R})]\,\chi(\mathbf{R}) = E\chi(\mathbf{R}) \tag{7}$$

Moreover, each electronic eigenvalue, $\varepsilon_n(\mathbf{R})$, will give rise to an electronic *surface*, and these surfaces are known as *Born-Oppenheimer surfaces*. Thus, the full internuclear potential for each electronic surface is given by $V_{\mathrm{NN}}(\mathbf{R}) + \varepsilon_n(\mathbf{R})$. On each Born-Oppenheimer surface, the nuclear eigenvalue problem can be solved, which yields a set of levels (rotational and vibrational in the nuclear motion). This is illustrated in the figure below:
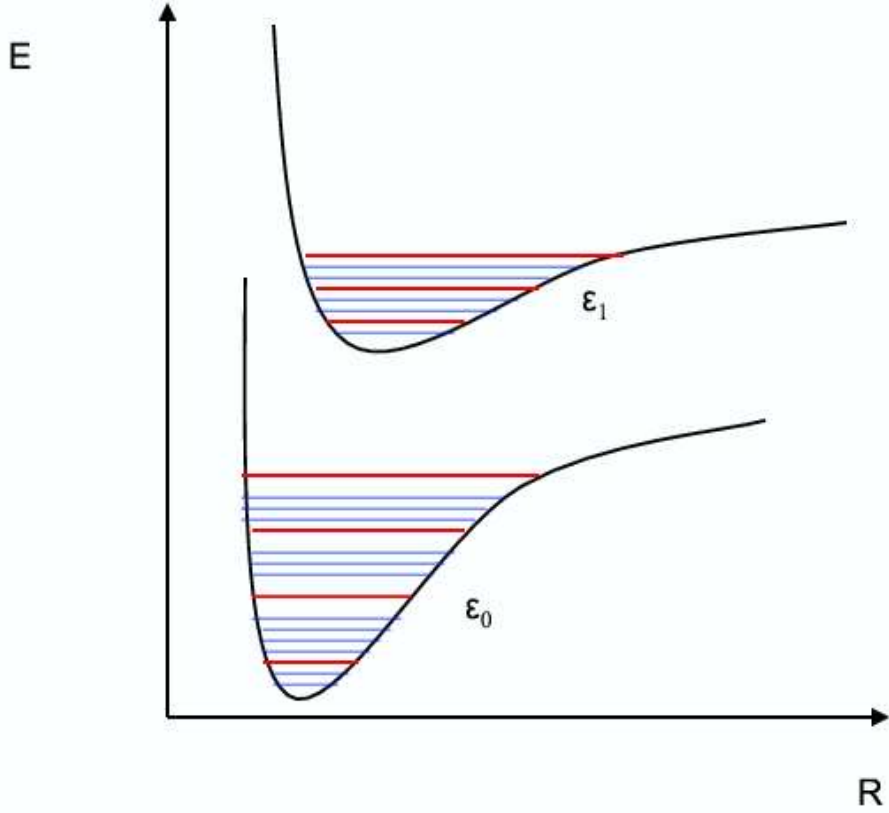
FIG. 1.

The Born-Oppenheimer surfaces are surfaces on which the nuclear dynamics is described by a time-dependent Schrödinger equation for the time-dependent nuclear wave function $X(\mathbf{R}, t)$:

$$[T_\mathrm{N} + V_\mathrm{NN}(\mathbf{R}) + \varepsilon_n(\mathbf{R})]\, X(\mathbf{R}, t) = i\hbar \frac{\partial}{\partial t} X(\mathbf{R}, t) \tag{8}$$

will evolve. The physical interpretation of Eq. (8) is that the electrons respond instantaneously to the nuclear motion, therefore, it is sufficient to obtain a set of instantaneous electronic eigenvalues and eigenfunctions at each nuclear configuration, $\mathbf{R}$ (hence the parametric dependence of $\phi_n(\mathbf{x}, \mathbf{R})$ and $\varepsilon_n(\mathbf{R})$ on $\mathbf{R}$). The eigenvalues, in turn, give a family of (uncoupled) potential surfaces on which the nuclear wave function can evolve. Of course, these surfaces can (and often do) become coupled by so called non-adiabatic effects, contained in the terms that have been neglected in the above derivation.

An important assumption of the Born-Oppenheimer approximation is that there are no excitations of the electrons among the various surfaces. Such excitations constitute non-adiabatic effects which are, therefore, neglected. As an example of a conditions in which this approximation is valid, consider a system at temperature T. If the electrons are in their ground state $\varepsilon_0(\mathbf{R})$, then, if $\varepsilon_1(\mathbf{R})$ denotes the first excitates state, there will be no excitations to this state if

$$|\varepsilon_1(\mathbf{R}) - \varepsilon_0(\mathbf{R})| \gg kT \tag{9}$$

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for all nuclear configurations. Without complete knowledge of these surfaces, it is not possible to know *a priori* if this condition will be satisfied, and there could be regions where the surfaces approach each other with an energy spacing close to kT. If the system visits such nuclear configurations, then the Born-Oppenheimer approximation will break down.
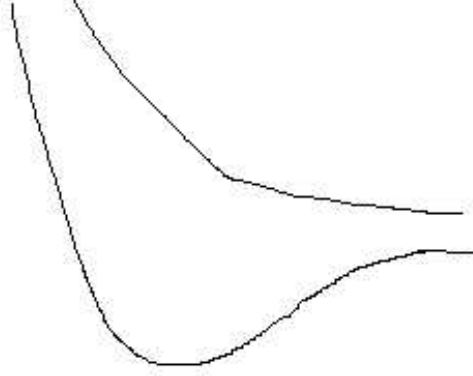

FIG. 2.

In many cases, non-adiabatic effects can be neglected, and we may consider motion *only* on the ground electronic surface described by:

$$[T_e + V_{ee}(\mathbf{r}) + V_{eN}(\mathbf{r}, \mathbf{R})]\,\phi_0(\mathbf{x}, \mathbf{R}) = \varepsilon_0(\mathbf{R})\phi_0(\mathbf{x}, \mathbf{R})$$

$$[T_N + \varepsilon_0(\mathbf{R}) + V_{NN}(\mathbf{R})]\,X(\mathbf{R}, t) = i\hbar\frac{\partial}{\partial t}X(\mathbf{R}, t) \tag{10}$$

Moreover, if nuclear quantum effects can be neglected, then we may arrive at classical nuclear evolution by assuming $X(\mathbf{R}, t)$ is of the form

$$X(\mathbf{R}, t) = A(\mathbf{R}, t)e^{iS(\mathbf{R}, t)/\hbar} \tag{11}$$

and neglecting all terms involving $\hbar$, which yields an approximate equation for $S(\mathbf{R}, t)$:

$$H_N(\nabla_1 S, ..., \nabla_N S, \mathbf{R}_1, ..., \mathbf{R}_N) + \frac{\partial S}{\partial t} = 0 \tag{12}$$

which is just the classical Hamiltonian-Jacobi equation with

$$H_N(\mathbf{P}_1, ..., \mathbf{P}_N, \mathbf{R}_1, ..., \mathbf{R}_N) = \sum_{I=1}^{N}\frac{\mathbf{P}_I^2}{2M_I} + V_{NN}(\mathbf{R}) + \varepsilon_0(\mathbf{R}) \tag{13}$$

denoting the classical nuclear Hamiltonian. The Hamilton-Jacobi equation is equivalent to classical motion on the ground-state surface, $E_0(\mathbf{R}) = \varepsilon_0(\mathbf{R}) + V_{NN}(\mathbf{R})$ given by

$$\dot{\mathbf{R}}_I = \frac{\mathbf{P}_I}{M_I}$$

$$\dot{\mathbf{P}}_I = -\nabla_I E_0(\mathbf{R}) \tag{14}$$

Note that the force $-\nabla_I E_0(\mathbf{R})$ contains a term from the nuclear-nuclear repulsion and a term from the derivative of the electronic eigenvalue, $\varepsilon_0(\mathbf{R})$. Because of the Hellman-Feynman theorem, the latter can be expressed as

$$\nabla_I \varepsilon_0(\mathbf{R}) = \langle \phi_0(\mathbf{R}) | \nabla_I H_{\mathrm{e}}(\mathbf{R}) | \phi_0(\mathbf{R}) \rangle \tag{15}$$

Equations (14) and Eq. (15) form the theoretical basis of the AIMD approach. The practical implementation of the AIMD method requires an algorithm for the numerical solution of Eq. (14) with forces obtained from Eq. (15) at each step of the calculation. Moreover, since an exact solution for the ground state electronic wave function, $|\phi_0(\mathbf{R})\rangle$ and eigenvalue, $\varepsilon_0(\mathbf{R})$ are not available, in general, it is necessary to introduce an approximation scheme for obtaining these quantities. This is the topic of the next section.

II. PROOF OF THE HELLMAN-FEYNMAN THEOREM

Consider a system with a Hamiltonian $H(\lambda)$ that depends on some parameters λ. Let $|\psi(\lambda)\rangle$ be an eigenvector of $H(\lambda)$ with eigenvalue $E(\lambda)$

$$H(\lambda)|\psi(\lambda)\rangle = E(\lambda)|\psi(\lambda)\rangle \tag{16}$$

We further assume that $|\psi(\lambda)\rangle$ is normalized so that

$$\langle \psi(\lambda)|\psi(\lambda)\rangle = 1 \tag{17}$$

The Hellman-Feynman theorem states that

$$\frac{dE}{d\lambda} = \left\langle \psi(\lambda) \left| \frac{dH}{d\lambda} \right| \psi(\lambda) \right\rangle \tag{18}$$

The proof of the Hellman-Feynman theorem is straightforward. We begin with the fact that

$$E(\lambda) = \langle \psi(\lambda)|H(\lambda)|\psi(\lambda)\rangle \tag{19}$$

Differentiating both sides yields

$$\frac{dE}{d\lambda} = \left\langle \psi(\lambda) \left| \frac{dH}{d\lambda} \right| \psi(\lambda) \right\rangle + \left\langle \frac{d\psi}{d\lambda} \left| H(\lambda) \right| \psi(\lambda) \right\rangle + \left\langle \psi \left| H(\lambda) \right| \frac{d\psi}{d\lambda} \right\rangle \tag{20}$$

Since $|\psi(\lambda)\rangle$ is an eigenvector of $H(\lambda)$, this can be written as

$$\frac{dE}{d\lambda} = \left\langle \psi(\lambda) \left| \frac{dH}{d\lambda} \right| \psi(\lambda) \right\rangle + E(\lambda) \left\langle \frac{d\psi}{d\lambda} \mid \psi(\lambda) \right\rangle + E(\lambda) \left\langle \psi \mid \frac{d\psi}{d\lambda} \right\rangle$$

$$\left\langle \psi(\lambda) \left| \frac{dH}{d\lambda} \right| \psi(\lambda) \right\rangle + E(\lambda) \left[\left\langle \frac{d\psi}{d\lambda} \mid \psi(\lambda) \right\rangle + \left\langle \psi \mid \frac{d\psi}{d\lambda} \right\rangle \right]$$

However, since $|\psi(\lambda)\rangle$ is normalized, we have, from the normalization condition:

$$\langle \psi(\lambda)|\psi(\lambda)\rangle = 1$$

$$\left\langle \frac{d\psi}{d\lambda} \mid \psi(\lambda) \right\rangle + \left\langle \psi \mid \frac{d\psi}{d\lambda} \right\rangle = 0$$

Hence, the term in square brackets vanishes, and we have

$$\frac{dE}{d\lambda} = \left\langle \psi(\lambda) \left| \frac{dH}{d\lambda} \right| \psi(\lambda) \right\rangle \tag{21}$$

which is just the Hellman-Feynman theorem.