# 1 Born-Oppenheimer Approximation

Consider the total Hamiltonian in this form

$$\hat{T}_{\text{nuc}} + \hat{H}_e$$

where $\hat{T}_{\text{nuc}}$ represents the kinetic energy operator of the nuclei, $\hat{H}_e$ includes the rest terms of the total Hamiltonian.

The nuclear motions are considered relatively slow compared to the electron motions. The nuclear positions serve as slowly changing external parameters. The total wave function can be expanded by electronic states, $\psi_i(\mathbf{r};\mathbf{R})$, times the wave function, $\chi_i(\mathbf{R},t)$, for the nuclear motion associated with the $i$th electronic state, and for fixed values of the nuclear coordinates, it can be considered as an "expansion coefficient" in an expansion that, in principle, is exact for a complete set of electronic states. (Do not completely understand)

$$\Psi(\mathbf{r},\mathbf{R},t) = \sum_i \chi_i(\mathbf{R},t)\psi_i(\mathbf{r};\mathbf{R})$$

Under adiabatic approximation, the electronic state is said to be unchanged as long as the nuclear motion can be considered as being sufficiently slow, which means no transitions among different electronic states happen (In certain conditions). The wave function in adiabatic approximation

$$\Psi_{\text{adia}}(\mathbf{r},\mathbf{R},t) = \chi(\mathbf{R},t)\psi_i(\mathbf{r};\mathbf{R})$$

where the subscript is ignored in $\chi(\mathbf{R},t)$ to coincide with the book notation.

$\psi_i(\mathbf{r})$ satisfies

$$\hat{H}_e\psi_i(\mathbf{r}) = E_i(\mathbf{R})\psi_i(\mathbf{r})$$

The dynamics of the total wave function in adiabatic approximation is

$$i\hbar\frac{\partial\chi(\mathbf{R},t)\psi_i(\mathbf{r};\mathbf{R})}{\partial t} = (\hat{T}_{\text{nuc}} + \hat{H}_e)\chi(\mathbf{R},t)\psi_i(\mathbf{r};\mathbf{R})$$
$$\psi_i(\mathbf{r};\mathbf{R})i\hbar\frac{\partial\chi(\mathbf{R},t)}{\partial t} = (\hat{T}_{\text{nuc}} + E_i(\mathbf{R}))\chi(\mathbf{R},t)\psi_i(\mathbf{r};\mathbf{R})$$

Times $\psi_i^*(\mathbf{r};\mathbf{R})$ by both sides,

$$i\hbar\frac{\partial\chi(\mathbf{R},t)}{\partial t} = \langle\psi_i(\mathbf{r};\mathbf{R})|\left(\hat{T}_{\text{nuc}}\right)|\psi_i(\mathbf{r};\mathbf{R})\rangle\,\chi(\mathbf{R},t) + E_i(\mathbf{R})\chi(\mathbf{R},t) \tag{1}$$

The nuclei kinetic operator has the form

$$\hat{T}_{\text{nuc}} = \sum_g \frac{\hat{P}_g^2}{2M_g} = -\sum_g \frac{\hbar^2}{2M_g}\nabla_g^2$$

Consider

$$\begin{aligned}
&\langle\psi_i|\left(\hat{T}_{\text{nuc}}\right)|\psi_i\rangle\,\chi(\mathbf{R},t)\\
&= -\sum_g \frac{\hbar^2}{2M_g}\langle\psi_i|\,\nabla_g^2\,|\psi_i\rangle\,\chi(\mathbf{R},t)\\
&= -\sum_g \frac{\hbar^2}{2M_g}\left[\nabla_g^2\chi(\mathbf{R},t) + 2\,\langle\psi_i|\,\nabla_g\,|\psi_i\rangle_0\,\nabla_g\chi(\mathbf{R},t) + \langle\psi_i|\,\nabla_g^2\,|\psi_i\rangle_0\,\chi(\mathbf{R},t)\right]\\
&= -\sum_g \frac{\hbar^2}{2M_g}\left[\nabla_g^2 + 2\,\langle\psi_i|\,\nabla_g\,|\psi_i\rangle_0\,\nabla_g + \langle\psi_i|\,\nabla_g^2\,|\psi_i\rangle_0\right]\chi(\mathbf{R},t)\\
&= \left[\hat{T}_{\text{nuc}} + \sum_g \langle\psi_i|\,\hat{P}_g\,|\psi_i\rangle_0\,\hat{P}_g/M_g + \langle\psi_i|\,\hat{T}_{\text{nuc}}\,|\psi_i\rangle_0\right]\chi(\mathbf{R},t)
\end{aligned}$$

where the subscript means to only act on the electronic states. Consider

$$\langle\psi_i|\,\hat{P}_g\,|\psi_i\rangle_0 = -i\hbar\,\langle\psi_i|\,\nabla_g\,|\psi_i\rangle_0 \tag{2}$$

If we take the electronic state to be real, (2) equals to 0. Since the expectation value of Hermitian operator is real, the left-hand side is a real number. The derivative of a real function is real, the right-hand side must be a complex number. Thus, they must both equal 0. $\langle\psi_i|\,\hat{T}_{\text{nuc}}\,|\psi_i\rangle_0$ is said to be very small compared to the electronic energy and may consequently be dropped. (1) can be written as

$$i\hbar\frac{\partial\chi(\mathbf{R},t)}{\partial t} = \left[\hat{T}_{\text{nuc}} + E_i(\mathbf{R})\right]\chi(\mathbf{R},t) \tag{3}$$

which is the Born-Oppenheimer approximation.