Born-Oppenheimer Approximation

Basic idea: electrons move much faster than ions. Therefore, it is tempting to approximate the eigenstates of electron + ions as

$$\Psi(r, R) = \phi_R \, \psi_R(r)$$

where r denotes e^- coordinates, and R denotes ions' coordinates.

The total Hamiltonian is

$$H = \sum_{ij} V^{\text{ion-ion}}(R_i - R_j) + \sum_{\alpha i} V^{\text{ion-e}}(r_\alpha - R_i)$$
$$+ \sum_{\alpha\beta} V^{e\text{-}e}(r_\alpha - r_\beta) + \sum_\alpha \frac{p_\alpha^2}{2m} + \sum_i \frac{P_i^2}{2M}$$

Due to wide separation in time scales for e^-s and ions, it is natural to ask if one can write down separate Schrodinger's eqns. for them. To do so, we follow the following trick.

$$H\,\psi = E\,\psi$$

$$\Rightarrow \int_r \psi^* H \psi = E \int_r \psi^* \psi$$

$$= E\,\Phi_R$$

The R.H.S. is suggestive that this is the schrodinger's eqn for ions. To make progress, we need to evaluate the L.H.S. $= \int_r \psi^* H \psi$

To simplify notation, lets consider the schrodinger's eqn. for e^-s at fixed value of ion's coordinates,

$$\left[V^{ion-e}_{(r,R)} + V^{e-e} + \sum_\alpha \frac{p_\alpha^2}{2m} \right] \psi_R(r) = E_e(R)\,\psi_R(r)$$

$$\Rightarrow \int \psi^* H \psi$$

$$= \left[E_e(R) + V^{ion-ion}_{(\{R\})} \right] \Phi_R$$

$$+ \int_r \psi^*_R(r) \sum_i \frac{P_i^2}{2M} \left[\psi_R(r)\,\Phi_R \right]$$

The second-term is what we need to focus on since it is not proportional to ϕ_R due to derivatives. Expanding, one finds three terms.

$$\int_r \psi^*_R(r) \frac{-\nabla_R^2 \psi_R(r)}{2M} \phi_R$$

$$+ \int_r \psi^*_R(r) \psi_R(r) \frac{-\nabla_R^2 \phi_R}{2M}$$

$$+ \frac{-2}{2M} \int_r \psi^*_R(r) \nabla_R \psi_R(r) \nabla_R \phi_R$$

Let's estimate the order of magnitude of these three terms.

We assume that ions are moving in a harmonic potential with potential energy $\frac{1}{2} M \omega^2 R^2$ and electrons form a Fermi surface with

Fermi energy $E_f \sim \frac{\hbar^2}{2ma^2}$ where a is the lattice spacing between ions.

Energy to displace ion by lattice spacing $\approx$ Energy to rearrange e^- wfn $\approx E_f$

$$\Rightarrow \quad M\omega^2 a^2 \sim E_f \sim \frac{\hbar^2}{2ma^2}$$

$$\Rightarrow \quad \omega \sim \sqrt{\frac{m}{M}} \, \frac{\hbar}{ma^2}$$

Further, the average displacement δ of ions may be estimated as

$$M\omega^2\delta^2 \sim \hbar\omega \Rightarrow \delta \sim a\left(\frac{m}{M}\right)^{1/4}$$

$$\sim 10^{-4} a \ll a$$

With these order of magnitude estimates lets return to the three terms in our earlier analysis.

lets express everything in terms of ε_F (fermi energy) and $\frac{m}{M}$ (the ratio of e^- to ion mass).

<u>first term</u>: $-\frac{\hbar^2\nabla_R^2}{2M}\psi_R\,\phi_R$.

since ψ_R is e^- wfn, $\nabla_R^2\psi_R$

$$\sim \frac{\psi_R}{a^2} \Rightarrow \hbar^2 \frac{-\nabla^2\psi_R}{2M}\phi_R \sim \frac{\hbar^2}{a^2 M}\psi\phi$$

$$\sim \frac{\hbar^2}{ma^2}\left(\frac{m}{M}\right)\psi\phi \sim \varepsilon_F \frac{m}{M}\psi\phi$$

<u>Second term</u>: $\psi_R \frac{-\hbar\nabla^2}{2M}\phi_R$

$$\Rightarrow \nabla^2\phi_R \sim \frac{\hbar^2}{2M\delta^2}\phi_R$$

$$\sim \frac{\hbar^2}{2Ma^2}\sqrt{\frac{M}{m}}\,\phi_R \sim \varepsilon_F\sqrt{\frac{m}{M}}\,\phi_R$$

$$\Rightarrow \psi_R - \frac{\hbar^2\nabla^2}{2M}\phi_R \sim \varepsilon_F\sqrt{\frac{m}{M}}\,\phi\,\psi$$

Third term: $-\dfrac{\hbar^2}{2M} \nabla_R \psi_R(r) \nabla_R \Phi_R$

$$\sim \frac{\hbar^2}{2M a \delta} \psi \phi$$

$$\sim \phi\psi \frac{\hbar^2}{2M a a} \left(\frac{M}{m}\right)^{1/4} \sim \varepsilon_F \left(\frac{m}{M}\right)^{3/4} \phi\psi$$

$\Rightarrow$ Second term $\gg$ Third term $\gg$ first term.

Keeping only the second term, we obtain the standard looking Schrodinger's eqn. for ions:

$$\left[\sum_i \frac{P_i^2}{2M} + E_e(R) + V^{\text{ion-ion}}\right] \phi(R)$$

$$= E \, \phi(R)$$

Therefore, we have succeded in separating ion's and e^-'s motions.