Tight-Binding

Hamiltonian for one-electron around a proton at site $\underline{R}_1$:

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{|r-\underline{R}_1|}$$

let $\varphi(r-\underline{R}_1)$ be a solution of $H\varphi = E\varphi$. with energy $E=E_0$

Consider now the Hamiltonian for one-electron around a proton at site $\underline{R}_1$ and another proton at site $\underline{R}_2$

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{|r-\underline{R}_1|} - \frac{e^2}{|\underline{r}-\underline{R}_2|}.$$

Assume that $|\underline{R}_1-\underline{R}_2|$ is large compared to the spatial extent of $\varphi(r)$. Then we can make use of the wavefunctions $\varphi(\underline{r}-R_1)$ and $\varphi(\underline{r}-R_2)$ to find the solution of

$$H\psi = E\psi$$

in terms of $\psi(r) = \alpha\,\varphi(\underline{r}-\underline{R}_1) + \beta\,\varphi(\underline{r}-\underline{R}_2)$ with

$$\alpha^2+\beta^2 = 1.$$

We now have to diagonalized the Hamiltonian suspended by the wave functions $\varphi(\underline{r}-\underline{R}_1)$ and $\varphi(\underline{r}-\underline{R}_2)$:

$$H = \begin{bmatrix} \langle\varphi(r-\underline{R}_1)|H|\varphi(r-\underline{R}_1)\rangle & \langle\varphi(r-\underline{R}_2)|H|\varphi(r-\underline{R}_1)\rangle \\ \langle\varphi(r-\underline{R}_1)|H\,\varphi(r-\underline{R}_2)\rangle & \langle\varphi(r-\underline{R}_2)|H|\varphi(\underline{r}-\underline{R}_2)\rangle \end{bmatrix}$$

and the equation to solve is

$$\begin{bmatrix} & H & \end{bmatrix}\begin{bmatrix} \varphi(\underline{r}-\underline{R}_1) \\ \varphi(\underline{r}-\underline{R}_2) \end{bmatrix} = E \begin{bmatrix} \varphi(\underline{r}-\underline{R}_1) \\ \varphi(\underline{r}-\underline{R}_2) \end{bmatrix}$$

We have to calculate:

$$\langle \varphi(\underline{r}-\underline{R}_1) | H | \varphi(\underline{r}-\underline{R}_1) \rangle =$$

$$= \langle \varphi(\underline{r}-\underline{R}_1) | -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{|\underline{r}-\underline{R}_1|} - \frac{e^2}{|\underline{r}-\underline{R}_2|} | \varphi(\underline{r}-\underline{R}_1) \rangle$$

$$= \langle \varphi(\underline{r}-\underline{R}_1 | -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{|\underline{r}-\underline{R}_1|} | \varphi(\underline{r}-\underline{R}_1) \rangle + \langle \varphi(\underline{r}-\underline{R}_1) | \frac{-e^2}{|\underline{r}-\underline{R}_2|} | \varphi(\underline{r}-\underline{R}_1) \rangle$$

$= E_0 +$ something small since $\varphi(\underline{r}-\underline{R}_1)$ is localized around $\underline{R}_1$ and $\frac{e^2}{|\underline{r}-\underline{R}_2|}$ is localized around $\underline{R}_2$

$\approx E_0$

$$\langle \varphi(\underline{r}-\underline{R}_1) | H | \varphi(\underline{r}-\underline{R}_2) \rangle =$$

$$= \langle \varphi(\underline{r}-\underline{R}_1) | -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{|\underline{r}-\underline{R}_1|} - \frac{e^2}{|\underline{r}-\underline{R}_2|} | \varphi(\underline{r}-\underline{R}_2) \rangle$$

$\equiv t_{12}$: this need not be a small number, since it depends on the overlap between $\varphi(\underline{r}-\underline{R}_1)$ and $\varphi(\underline{r}-\underline{R}_2)$.

With analogous expressions for $\langle \varphi(\underline{r}-\underline{R}_2) | H | \varphi(\underline{r}-\underline{R}_2) \rangle$ and $\langle \varphi(\underline{r}-\underline{R}_2) | H | \varphi(\underline{r}-\underline{R}_1) \rangle$.

We then have:

$$H = \begin{bmatrix} E_0 & t_{12} \\ t_{12} & E_0 \end{bmatrix}$$

Consider now the Hamiltonian of one-electron with three protons at sites $\underline{R}_1$, $\underline{R}_2$, and $\underline{R}_3$.

The Hamiltonian in the basis of $\varphi(\underline{r}-\underline{R}_1)$, $\varphi(\underline{r}-\underline{R}_2)$, $\varphi(\underline{r}-\underline{R}_3)$ is:

$$H=\begin{bmatrix} \langle\varphi(\underline{r}-\underline{R}_1)|H|\varphi(\underline{r}-\underline{R}_1)\rangle & \langle\varphi(\underline{r}-\underline{R}_2)|H|\varphi(\underline{r}-\underline{R}_1)\rangle & \langle\varphi(\underline{r}-\underline{R}_3)|H|\varphi(\underline{r}-\underline{R}_1)\rangle \\ \langle\varphi(\underline{r}-\underline{R}_1)|H|\varphi(\underline{r}-\underline{R}_2)\rangle & \langle\varphi(\underline{r}-\underline{R}_2)|H|\varphi(\underline{r}-\underline{R}_2)\rangle & \langle\varphi(\underline{r}-\underline{R}_3)|H|\varphi(\underline{r}-\underline{R}_2)\rangle \\ \langle\varphi(\underline{r}-\underline{R}_1)|H|\varphi(\underline{r}-\underline{R}_3)\rangle & \langle\varphi(\underline{r}-\underline{R}_2)|H|\varphi(\underline{r}-\underline{R}_3)\rangle & \langle\varphi(\underline{r}-\underline{R}_3)|H|\varphi(\underline{r}-\underline{R}_3)\rangle \end{bmatrix}$$

$\langle\varphi(\underline{r}-\underline{R}_1)|H|\varphi(\underline{r}-\underline{R}_1)\rangle =$

$$=\langle\varphi(\underline{r}-\underline{R}_1)\left|-\frac{\hbar^2}{2m}\nabla^2-\frac{e^2}{|\underline{r}-\underline{R}_1|}-\frac{e^2}{|\underline{r}-\underline{R}_2|}-\frac{e^2}{|\underline{r}-\underline{R}_3|}\right|\varphi(\underline{r}-\underline{R}_1)\rangle$$

$$= E_0 + \langle\varphi(\underline{r}-\underline{R}_1)\left|-\frac{e^2}{|\underline{r}-\underline{R}_2|}-\frac{e^2}{|\underline{r}-\underline{R}_3|}\right|\varphi(\underline{r}-\underline{R}_1)\rangle$$

$\approx E_0$ localized around $\underline{R}_1$; localized around $\underline{R}_2$; localized around $\underline{R}_3$; localized around $\underline{R}_1$ $\Rightarrow$ integral is small

$\langle\varphi(\underline{r}-\underline{R}_1)|H|\varphi(\underline{r}-\underline{R}_2)\rangle =$

$$=\langle\varphi(\underline{r}-\underline{R}_1)\left|-\frac{\hbar^2}{2m}\nabla^2-\frac{e^2}{|\underline{r}-\underline{R}_1|}-\frac{e^2}{|\underline{r}-\underline{R}_2|}-\frac{e^2}{|\underline{r}-\underline{R}_3|}\right|\varphi(\underline{r}-\underline{R}_2)\rangle$$

$$= t_{12} + \langle\varphi(\underline{r}-\underline{R}_1)\left|-\frac{e^2}{|\underline{r}-\underline{R}_3|}\right|\varphi(\underline{r}-\underline{R}_2)\rangle$$

$\approx t_{12}$

localized around $\underline{R}_1$; localized around $\underline{R}_3$; localized around $\underline{R}_2$ $\Rightarrow$ integral is small.

The Hamiltonian is then:

$$H=\begin{bmatrix} E_0 & t_{21} & t_{31} \\ t_{12} & E_0 & t_{32} \\ t_{13} & t_{23} & E_0 \end{bmatrix}$$