## Ex: Hückel theory

$$\phi_n^*(\vec{r}) = \phi_n(\vec{r})$$

(1) $$h_{nn} = -\frac{1}{2}\int d\vec{r}\, \phi_n(\vec{r})\, \nabla^2_{\vec{r}}\phi_n(\vec{r}) + \int d\vec{r}\, v_{ne}(\vec{r})\, \phi_n^2(\vec{r})$$

where $$\phi_n(\vec{r}) \equiv \phi_n(x,y,z) = \frac{1}{\sqrt{\pi}}\, e^{-\sqrt{(x-na)^2+y^2+z^2}}$$

Let $$\tilde{\phi}(x,y,z) = \frac{1}{\sqrt{\pi}}\, e^{-\sqrt{x^2+y^2+z^2}}.$$

Since $\phi_n(\vec{r}) = \tilde{\phi}(x-na,y,z)$, $$\nabla^2_{\vec{r}}\phi_n(\vec{r}) = \nabla^2_{\vec{r}}\left(\tilde{\phi}(x-na,y,z)\right) = \nabla^2_{\vec{r}\,'}\tilde{\phi}(\vec{r}\,')$$

where $\vec{r}\,' \equiv (x-na, y, z) = (x', y', z')$. Therefore

$$-\frac{1}{2}\int d\vec{r}\, \phi_n(\vec{r})\, \nabla^2_{\vec{r}}\phi_n(\vec{r}) = -\frac{1}{2}\int d\vec{r}\,'\, \tilde{\phi}(\vec{r}\,')\, \nabla^2_{\vec{r}\,'}\tilde{\phi}(\vec{r}\,') \longleftarrow \text{does not depend on } n.$$

Moreover, $$\int d\vec{r}\, v_{ne}(\vec{r})\, \phi_n^2(\vec{r}) = \int d\vec{r}\,'\, \underbrace{v_{ne}(x'+na, y', z')}_{v_{ne}(\vec{r}\,')}\, \tilde{\phi}^2(\vec{r}\,')$$ periodicity!

$$\| $$

$$\int d\vec{r}\,'\, v_{ne}(\vec{r}\,')\, \tilde{\phi}^2(\vec{r}\,')$$ does not depend on $n$.

Conclusion:

$$\boxed{\alpha = -\frac{1}{2}\int d\vec{r}\, \tilde{\phi}(\vec{r})\, \nabla^2_{\vec{r}}\tilde{\phi}(\vec{r}) + \int d\vec{r}\, v_{ne}(\vec{r})\, \tilde{\phi}^2(\vec{r})} = h_{nn}$$

(2) $$h_{n(n+1)} = -\frac{1}{2}\int d\vec{r}\, \phi_n(\vec{r})\, \nabla^2_{\vec{r}}\phi_{n+1}(\vec{r}) + \int d\vec{r}\, v_{ne}(\vec{r})\, \phi_n(\vec{r})\, \phi_{n+1}(\vec{r}).$$

Let $$\begin{cases} \tilde{\phi}_-(x,y,z) = \tilde{\phi}(x-a,y,z) \\ \vec{r}\,' \equiv (x-na,y,z) = (x',y',z') \end{cases} \Rightarrow \nabla^2_{\vec{r}}\phi_{n+1}(\vec{r}) = \nabla^2_{\vec{r}}\left(\tilde{\phi}_-(x-na,y,z)\right) = \nabla^2_{\vec{r}\,'}\tilde{\phi}_-(\vec{r}\,')$$

$$\Rightarrow h_{n(n+1)} = -\frac{1}{2}\int d\vec{r}\,'\, \tilde{\phi}(\vec{r}\,')\, \nabla^2_{\vec{r}\,'}\tilde{\phi}_-(\vec{r}\,') + \int d\vec{r}\,'\, \underbrace{v_{ne}(x'+na, y', z')}_{v_{ne}(\vec{r}\,')}\, \tilde{\phi}(\vec{r}\,')\, \tilde{\phi}_-(\vec{r}\,')$$

$$\Rightarrow \boxed{h_{n(n+1)} = \beta = -\frac{1}{2}\int d\vec{r}\, \tilde{\phi}(\vec{r})\, \nabla^2_{\vec{r}}\tilde{\phi}_-(\vec{r}) + \int d\vec{r}\, v_{ne}(\vec{r})\, \tilde{\phi}(\vec{r})\, \tilde{\phi}_-(\vec{r})}$$

(3) $$h_{nm} = -\frac{1}{2}\int d\vec{r}\, \phi_n(\vec{r}) \underbrace{\nabla^2_{\vec{r}}\, \phi_m(\vec{r})}_{\text{assumed to spread over space roughly like } \phi_m(\vec{r})} + \int d\vec{r}\, v_{ne}(\vec{r}) \underbrace{\phi_n(\vec{r})\, \phi_m(\vec{r})}_{\to 0 \text{ if } n \text{ and } m \text{ do not correspond to neighbors.}}$$

$$\begin{aligned} h_{nm} &= \beta \quad \text{if } n \text{ and } m \text{ are neighbors} \Leftrightarrow n = m+1 \text{ or } n = m-1 \\ &= \alpha \quad \text{if } n = m \\ &= 0 \quad \text{otherwise} \end{aligned}$$

<u>Conclusion:</u> $$\boxed{h_{nm} = \alpha\delta_{nm} + \beta\left(\delta_{n(m+1)} + \delta_{n(m-1)}\right)}$$