Lesson 3

Winter 2019

Single-center expansion

- Originated in atomic calculations from 50' and 60' of 20-th century
- First applied to a diatomic system in 1960
- In bound-state problem it was abandoned to multicenter bases, STO, GTO
- In scattering calculation it is still active
- Most of the variational method apply SCE in the asymptotic region
- Present derivation employs anisotropic local potential $V(\vec{r})$ and non-local $W(\vec{r},\vec{r}')$

$$V(\vec{r},\vec{r}') = \delta(\vec{r}-\vec{r}')\, V_{loc}(\vec{r}) + W(\vec{r},\vec{r}')$$

Examples of $W(\vec{r},\vec{r}')$ .... exchange interaction in HF approximation

.... complicated correlation interaction, reflecting molecular response to a presence of the incoming electron

Schrödinger equation in 3D

$$\left[-\frac{1}{2}\nabla^2 - E\right]\psi(\vec{r}) = -V_{loc}(\vec{r})\psi(\vec{r}) - \int d^3r'\, W(\vec{r},\vec{r}')\psi(\vec{r}') \qquad (1)$$

- After choosing the expansion center, we expand to partial waves:

$$\psi(\vec{r}) = \frac{1}{r}\sum_{\ell'm'} u_{\ell'm'}(r)\, Y_{\ell'm'}(\hat{r}) \qquad (2)$$

- Substitute into (1) and project onto $\langle Y_{\ell m}|$. We apply $-2r\int d\hat{r}\, Y_{\ell m}(\hat{r})$ /
- Identity $-\frac{1}{2}\nabla^2\psi(\vec{r}) = \frac{1}{r}\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{\hat{L}^2}{2r^2}\right](r\psi(r,\vartheta,\varphi))$
- Coupled set of integro-differential equations:

$$\left[\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + k^2\right] u_{\ell m}(r) = 2\sum_{\ell'm'} V_{\ell m}^{\ell'm'}(r)\, u_{\ell'm'}(r) + 2\sum_{\ell'm'}\int_0^\infty dr'\, W_{\ell m}^{\ell'm'}(r,r')\, u_{\ell'm'}(r)$$

$$V_{\ell m}^{\ell'm'}(r) \equiv \int d\hat{r}\, Y_{\ell m}^*(\hat{r})\, V_{loc}(\vec{r})\, Y_{\ell'm'}(\hat{r})$$

$$W_{\ell m}^{\ell'm'}(r,r') \equiv rr'\int d\hat{r}\, d\hat{r}'\, Y_{\ell m}^*(\hat{r})\, W(\vec{r},\vec{r}')\, Y_{\ell'm'}(\hat{r}')$$

- In the following we neglect the non-local term $W(\vec{r},\vec{r}') = 0$

Moreover, $(lm) \equiv i$, $(l'm') \equiv j$, ...

- Mathematics (for l_{max} we got $N = (l_{max}+1)^2$ equations)

- A solution is specified by chosing 2 out of 4 boundary conditions (BC)

$u_i(0)$; $u_i'(0)$; $u_i(\infty)$, $u_i'(\infty)$

$$\left[\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} + k^2\right] u_i(r) = 2 \sum_k V_{ik}(r)\, u_k(r)$$

- Without chosing BC's we have $2N$ solutions; N regular and N irregular
- Substitution $\psi = \frac{1}{r}\sum_i u_i Y_i$ fixes $u_i(0) = 0$. Therefore we have N indep. solutions that we put into columns of $u_{ij}(r)$

$$\left[\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{2r^2} + k^2\right] u_{ij}(r) = 2 \sum_k V_{ik}(r)\, u_{kj}(r)$$

At the begining we set out to find 1 solution of the Schr. equation, but mathematics told us we have N indep. solutions

$$\psi_j(\vec{r}) = \frac{1}{r}\sum_i u_{ij}(r)\, Y_i(\hat{r})$$

In theory there is ∞ solutions as $N = (l_{max}+1)^2$ is the size of our angular space.

Question: Which of the $\psi_j(\vec{r})$ solutions is the scattering solution having asymptotics

$$\psi^{(+)}_{\vec{k}}(\vec{r}) \xrightarrow{r\to\infty} e^{i\vec{k}\cdot\vec{r}} + f(\vartheta,\varphi)\frac{e^{ikr}}{r} \quad ?$$

Answer: None. But a proper linear combination (which is again a solution of the Schröd. equation) might have the proper asymtotics.

$$\psi^{(+)}_{\vec{k}}(\vec{r}) = \sum_j a_j \psi_j(\vec{r})$$

Proof and some notes: For $r\to\infty$ $u_{ij}(r)$ is a linear combination of the two solutions

$$u_{ij}(r) \xrightarrow{r\to\infty} e^{-i(kr - l_i\frac{\pi}{2})} - e^{i(kr - l_i\pi/2)} S_{ij}$$

Single-center expansion (continued)

We want $\psi_{\vec{k}}^{(+)}(\vec{r}) = \sum_j a_j \psi_j(\vec{r}) = \frac{1}{r}\sum_{ij} a_j u_{ij}(r) Y_i(\hat{r}) \xrightarrow{r\to\infty} e^{i\vec{k}\cdot\vec{r}} + f(\vartheta,\varphi)\frac{e^{ikr}}{r}$

$$\frac{1}{r}\sum_{ij} a_j Y_i(\hat{r})\left[e^{-i(kr-l_i\pi/2)}\delta_{ij} - e^{i(kr-l_i\pi/2)} S_{ij}\right] = \frac{4\pi}{kr}\sum_i i^{l_i}\left[e^{i(kr-l_i\pi/2)} - e^{-i(kr-l_i\pi/2)}\right]\frac{1}{2i} Y_i^*(\hat{k}) Y_i(\hat{r}) + f(\vartheta,\varphi)\frac{e^{ikr}}{r}$$

$$a_j = \frac{2\pi i}{k} i^{l_j} Y_j^*(\hat{k})$$

$$e^{i\vec{k}\cdot\vec{r}} = \frac{4\pi}{kr}\sum_{lm} j_l(kr)\, i^l Y_{lm}^*(\hat{k}) Y_{lm}(\hat{r})$$

$$f(\vartheta,\varphi) = -\frac{2\pi i}{k}\sum_{ij} i^{l_j - l_i} Y_i(\hat{r})\left[S_{ij} - \delta_{ij}\right] Y_j^*(\hat{k})$$

- Rotational period of molecule at room temperature $\geq 10^{-12}$ s
- Interaction time of 1eV electron with a molecule in region of ~ 20 Å $\sim 10^{-14} - 10^{-15}$ s
- We can approximate the molecule as rotationally fixed, described by random orientations
- Integral cross section σ is computed by integration ~~over~~ of $|f(\vartheta,\varphi)|^2$ over $\hat{r}$ and averaging $\frac{1}{4\pi}\int d\hat{k}$ over $\hat{k}$:

$$\sigma = \frac{1}{4\pi}\int d\hat{k}\int d\hat{r}\, |f(\vartheta,\varphi)|^2 \;;\; |f(\vartheta,\varphi)|^2 = \frac{4\pi^2}{k^2}\sum_{\substack{i,j\\ m,n}}\left(Y_i(\hat{r})\underbrace{\left[S_{ij}-\delta_{ij}\right]}_{T_{ij}} Y_j^*(\hat{k})\right)\left(Y_m^*(\hat{r})\left[S_{mn}-\delta_{mn}\right]^* Y_n(\hat{k})\right)$$

$$\sigma = \frac{\pi}{k^2}\sum_{ij}|S_{ij}-\delta_{ij}|^2 = \frac{\pi}{k^2}\sum_{ij}|T_{ij}|^2$$

- Diagonalization of $S = U\Lambda U^\dagger$; $\Lambda_k = e^{2i\delta_k}$; $S_{ij} = \sum_k U_{ik} e^{2i\delta_k} U_{jk}^*$

  δ_k ... eigenphase shifts

$$\sigma = \frac{\pi}{k^2}\sum_{ij}(S_{ij}-\delta_{ij})(S_{ij}-\delta_{ij})^* = \frac{\pi}{k^2}\sum_{ij}\left[\sum_k U_{ik}(e^{2i\delta_k}-1)U_{jk}^*\right]\left[\sum_l U_{il}^*(e^{2i\delta}-1)^* U_{jl}\right]$$

$$\sigma = \frac{\pi}{k^2}\sum_k |e^{2i\delta_k}-1|^2 = \frac{4\pi}{k^2}\sum_k \sin^2\delta_k$$

Similar to the spherical problem, but here in terms of the eigenphases!

Generalized unitarity limit