Lecture Wednesday 3. October 2007

Topics: Configuration Interaction, Configuration Mixing

Comments

Preliminary version

Expansion of a function (Q.M. - or Fourier Series ......) Two "variables"

Configuration mixing $\quad \Psi(1,2) \equiv \Psi(r_1, r_2)$

any $\underbrace{\varphi(x) = \sum_{i=0}^{\infty} c_i \varphi_i(x)}$ ..... $\to \varphi(a,x) = \sum' c_i(a) \varphi_i(x)$

$\to \varphi_a(x) = \sum c_i^{(a)} \varphi_i(x)$

$\Psi(1,2)$ (atomic problem; $\varphi_{n\ell}(\vec{r})$ are known orbitals (H-F, or SCF)

ANALOGY

$$\Psi(1,2) = \sum_{n\ell} c_{n\ell}(1) \varphi_{n\ell}(2) \quad \ldots\ldots$$

(SCHEMATIC) $\quad$ function of $\vec{r}_1$

$$c_{n\ell}(\vec{r}_1) = \sum' d_{n'\ell'}^{(n\ell)} \varphi_{n'\ell'}(\vec{r}_1)$$

Expansion "technique" thus lead to

$$\Psi(1,2) = \sum_{(n\ell)}' \sum_{(n'\ell')}' d_{n'\ell'}^{(n\ell)} \underbrace{\varphi_{n'\ell'}(\vec{r}_1) \varphi_{n\ell}(\vec{r}_2)}_{\text{configurations}}$$

$$\Psi(1,2) = \sum_{(nl)} \sum_{(n'l')} d^{(nl)}_{n'l'} \underbrace{\varphi_{n'l'}(\vec{r}_1)\, \varphi_{nl}(\vec{r}_2)}_{\text{configurations}}$$

$$\Psi(1,2) = \sum_{\alpha,\beta} a_{\alpha\beta}\, \varphi_\alpha(1)\, \varphi_\beta(2) \qquad \alpha \equiv (n, l_{\wedge m})$$

$$\Psi(1,2,3) = \sum_{\alpha\beta\gamma} a_{\alpha\beta\gamma}\, \varphi_\alpha(1)\, \varphi_\beta(2)\, \varphi_\gamma(3)$$

[should be properly antisymmetrized
Angular momentum must be done consistently ......

How to find $a_{\alpha,\beta\ldots\omega}$?

$\Psi(\ldots\ldots) = \sum c_K \, \Phi_K \qquad \Phi_K = \varphi_\alpha(1) \ldots\ldots \varphi_\nu(N)$

$H = T_i + V_i + \sum_{\substack{\text{pairs} \\ i\,j}} \frac{e^2}{|r_i - r_j|}$ Orbitals obtained from this !!

To obtain the orbitals, WE ASSUMED that

$\Psi \equiv \Phi_0$ (the lowest state ....)

And this is the basis of "mixing"

— but how to mix ?

$|K\rangle$ ..... H ... $\langle K'|H|K\rangle$ a matrix

finite number (includes a cut-off)

$$\begin{pmatrix} \langle K'|H|K\rangle & \cdots \\ & \cdots \\ & \cdots \end{pmatrix} \begin{pmatrix} \vdots \\ c_K \\ \vdots \end{pmatrix} = E \begin{pmatrix} \vdots \\ c_K \\ \vdots \end{pmatrix}$$

Diagonalization of the Hamilton matrix

Nuclear Phys. Atomic. Phys, Quant Chemistry

Comment ... the $e^{i\alpha}$ is an eigenvalue ... $\alpha\beta\gamma\delta$