

MSc Thesis

~~Our main interest is finding approximately solutions to the Dirac-Breit Hamiltonian for a many electron system.~~

(i) Dirac Hamiltonian

The total Dirac-Breit Hamiltonian for a many electron system has two terms: one-e-part consisting of kinetic energy, mass energy and nuclear attraction:

$$\hat{H}_{DB}(r_i) = c \alpha_i \cdot \vec{p}_i + c^2 (f_i - 1) + V_{nuc}(r_i)$$

where, for a point nucleus, $V_{nuc}(r_i) = -\frac{q}{r_i}$ and we have and a two-electron part, consisting of Coulomb repulsion term and Breit interaction.

rest mass energy

$$H_{DB} = \sum_{ij} \frac{1}{r_{ij}} + \sum_{ij} B_{ij}$$

In the low frequency limit,

$$B_{12} = \frac{-1}{(2\gamma_2)} \left\{ \bar{\alpha}_1 \bar{\alpha}_2 + \frac{[\bar{\alpha}_1 \cdot \bar{\alpha}_{12} (\bar{\epsilon}_1 \cdot \bar{\epsilon}_{12})]}{\gamma_{12}} \right\}$$

Dirac operators α and β are expressed by matrices

$$\alpha = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix} \quad \text{and} \quad \beta = \begin{pmatrix} I & 0 \\ 0 & -E \end{pmatrix} \quad \text{where } \vec{\sigma} \text{ stands for three Pauli matrices}$$

Atomic units ($e = \hbar = m = 1$) will be used throughout this thesis unless otherwise explicitly mentioned otherwise.

It will not be consider breit interaction for the rest of this discussion.

(4) Hartree-Fock equation

We are interested : finding a set of spin orbitals $\{\chi_a\}$ such that the Slater determinant formed from these spin orbitals

$$|\Psi_0\rangle = |x_1 x_2 \dots x_a x_b \dots x_n\rangle$$

is the best approximation to the ground state of the system.

The total energy is given by

$$E_0 = \langle \Psi_0 | H | \Psi_0 \rangle = \sum_a \langle a | h | a \rangle + \frac{1}{2} \sum_{ab} \langle ab | hab \rangle$$

where, $\langle i | h | j \rangle = \langle x_i | h | x_j \rangle$

$$= \int dx_1 dx_2 x_i^*(s_1) h(s_1) x_j(s_1)$$

$$\langle ij | kl \rangle = \langle x_i x_j | x_k x_l \rangle$$

$$= \int dx_1 dx_2 x_i^*(x_1) x_j^*(x_2) r_{12}^{-1} x_k(x_1) x_l(x_2)$$

$$\langle ij || kl \rangle = \langle ij | kl \rangle - \langle ij | lk \rangle$$

~~Ans~~

We can ~~approximately~~^{now} vary the spin orbitals (χ_a), ~~and~~^{choose} ~~them only to~~ such that they remain orthonormal,

$$\langle \chi_a | \chi_b \rangle = \delta_{ab}$$

until the energy E_0 is minimum. ~~by~~^{that} of the corresponding spin orbitals as the best approximation to the ground state of the system

This equation is called the Hartree-Fock Integro-differential equation.

$$h(1) \chi_a(1) + \sum_{b \neq a} \left[\int dx_2 |\chi_b(2)|^2 r_{12}^{-1} \right] \chi_a(1) - \sum_{b \neq a} \left[\int dx_2 \chi_b^*(2) \chi_a(2) r_{12}^{-1} \right] \chi_b(1) = \epsilon_a \chi_a(1)$$

Where h is the one electron operator.

The two summation terms in eqn ~~that~~ represent electron-electron interaction.

The first is the coulomb term which can be interpreted as the average potential acting on electron χ_a from the $(N-1)$ other electrons.

$$f(1) = \int dx_2 |\chi_b(2)|^2 r_{12}^{-1}$$

is defined as the coulomb operator.

The second term is called the exchange term which arises from the antisymmetric nature of the Slater determinant. It is due to a quantum phenomenon and therefore does not have a simple classical interpretation.

~~We can write the above the less, we can write the Hartree-Fock integro-differential equation as an eigenvalue equation.~~

$$\rightarrow [h(1) + \sum_{b \neq a} g_b(1) - \sum_{b \neq a} K_b(1)] \chi_a(1) = E_a \chi_a(1)$$

provided

$$g_b(1) \chi_a(1) = \left[\int d\tau_2 \chi_b^*(\tau) \tau_{12}^{-1} \chi_a(\tau) \right] K_b(1)$$

which involves an 'exchange' of electron 1 and 2

compared to

$$g_b(1) \chi_a(1) = \left[\int d\tau_2 \chi_b^*(\tau_2) \tau_{12}^{-1} \chi_b(\tau_2) \right] \chi_a(1)$$

Since: $[g_a(1) - K_a(1)] \chi_a(1) \approx 0$

we can add this to to obtain the usual form
of the Hartree-Fock equation

$$f[\chi_a] = E_a [\chi_a]$$

where $f(1) = h(1) + \sum_b [g_b(1) - K_b(1)]$

(iii) Interpretation of solutions of Hartree-Fock equations

The orbital energies can be expressed as,

$$\epsilon_i = \langle x_i | f | x_i \rangle \quad \cancel{\approx E_{\text{Hartree}}}$$

$$= \langle x_i | h^+ + \sum_b (g_b - k_b) | x_i \rangle.$$

$$= \langle i | h | i \rangle + \sum_b (g_b | i_b \rangle - \langle i_b | k_b \rangle)$$

$$= \langle i | h | i \rangle + \sum_b \langle i_b | k_b \rangle$$

If we add up all the orbital energies, we get

$$\sum_a \epsilon_a = \sum_a \langle a | h | a \rangle + \sum_{ab} \epsilon_b \langle a_b | k_b \rangle$$

Comparing this to $E_0 = \left(\frac{1}{2} \right) \sum_a \epsilon_a \rightarrow$ we

can see that $E_0 + \sum_a \epsilon_a$

~~The Orbital Energy Calc actually gives~~

Now, ~~assume~~ given a sige determined $I^{N-1} \Psi_{01}$, the ionization potential to produce an $(N-1)e^-$ sige. $\Delta I^{N-1} \Psi_{01}$ by removing one electron from x_a is given by

$$= N^{-1} E_a - N E_0$$

$$= \sum_a \epsilon_a + \frac{1}{2} \sum_{ab} \epsilon_b \langle a_b | k_b \rangle$$

$$= \langle a | h | a \rangle - \frac{1}{2} \sum_b \epsilon_b \langle a_b | k_b \rangle$$

$$= -\langle a | h | a \rangle - \frac{1}{2} \sum_c \langle c | h | c \rangle + \frac{1}{2} \sum_b \langle ab | h | ab \rangle$$

$$= -\langle a | h | a \rangle - \sum_b \langle ab | h | ab \rangle$$

$$= -E_a$$

Therefore, the orbital energies are the negative of ionisation potentials to remove the corresponding electrons (Hoopman's theorem).

~~This~~ all this diffn is because we have not solved the exact electronic Schrodinger equation

$$H |\Psi_0\rangle = E_0 |\Psi_0\rangle$$

but rather we have used the variational principle to find an approximate solution which are exact solutions of an Hamiltonian given by

$$H_0 = \sum_{i=1}^n f(i)$$

(iv)

Restricted
spin orbitals.

Closed shell Hartree Fock \rightarrow the Boston

In this following discussion, we are only concerned with restricted spin closed shell orbitals, that is, we are only allowed to have an even number of electrons with all c^- paired such that all spatial orbitals are doubly occupied.

\Rightarrow The restricted set of spin orbitals have the form

$$\chi_i(x) = \begin{cases} \psi_j(z) \alpha(\omega) \\ \psi_j(z) \beta(\omega) \end{cases}$$

Using the above, we can integrate out the spin function to give the following closed shell equations.

$$f(l) \psi_j(l) = \epsilon_j \psi_j(l)$$

$$f(l) = h(l) + \sum_a \frac{1}{2} 2 J_{ab}(l) - K_a(l)$$

$$J_{ab}(l) = \int d\tau_2 \psi_a^*(z) \tau_{12}^{-1} \psi_b(z)$$

$$K_a(l) \psi_i(l) = \left[\int d\tau_2 \psi_a^*(z) \tau_{12}^{-1} \psi_i(z) \right] \psi_a(l)$$

$$f_0 = 2 E_{baa} + E_a E_b 2 J_{ab} - K_{ab}$$

(V) Introduction of Basis: Nathan for my

Introduce ~~a~~ K basis functions $\{\phi_p(x)\}_{p=1}^K$

such that

$$\psi_i = \sum_{p=1}^K c_{pi} \phi_p$$

Substituting this into () gives,

$$f(1) \approx \sum_i c_{ri} \phi_r(1) = \xi_i \sum_i c_{ri} \phi_r(1)$$

Multiplying $\phi_p^*(1)$ on the left and integrating, we get

$$\begin{aligned} \xi_i c_{ri} \int dr_1 \phi_p^*(1) f(1) dr_1 \\ = \xi_i c_{ri} \int dr_1 \phi_p^*(1) \phi_r(1) \end{aligned}$$

Define ii) $S_{pq} = \int dr_1 \phi_p^*(1) \phi_q(1)$ called the overlap matrix. It is a $K \times K$ Hermitian matrix with diagonal elements unity and $0 \leq S_{pq} \leq 1$.

Since the basis functions are generally normalized and linearly independent but not orthogonal.

$$(ii) F_{pq} = \int dr_1 \phi_p^*(1) f(1) \phi_q(1)$$

called the force matrix.

With these () can be written as

$$\sum_i F_{pq} c_{ri} = \xi_i \sum_i S_{pq} c_{ri}, i = 1, 2, \dots, K$$

or more compactly,

$$FC = SC \alpha$$

This is called the Lanthan operations.

where C_i KKR man. of expansion coefficients α_i

$$C = \begin{pmatrix} C_1 & C_2 & \cdots & C_K \\ C_1 & C_2 & \cdots & C_K \\ \vdots & & & \\ C_1 & C_2 & \cdots & C_K \end{pmatrix}$$

and α is a diagonal matrix of orbital energies ϵ_i ,

$$\alpha = \begin{pmatrix} \epsilon_1 & 0 & & \\ 0 & \epsilon_2 & & \\ & & \ddots & \\ 0 & 0 & \cdots & \epsilon_K \end{pmatrix}$$

(iv) Charge density

prob. τ finds an electron in a volume element dr at point r is $|Y_{\alpha}(r)|^2 dr$.

therefore, the total charge density:

$$\rho(r) = 2 \sum_{\alpha=1}^{N_2} |Y_{\alpha}(r)|^2$$

$$\text{and } \int \rho(r) dr = 2 \sum_a^{N_2} \int dr |Y_{\alpha}(r)|^2 = 2 \sum_a^{N_2} 1 = N$$

Integrate the basis function into the same grid

$$P(r) = \sum_{\mu\nu} P_{\mu\nu} \phi_{\mu}(r) \phi_{\nu}^*(r)$$

where $P_{\mu\nu} = 2 \sum_{a=1}^{N/2} C_{\mu a} C_{\nu a}^*$ is called the density matrix.

Since P is directly related to the expansion coefficients C , the spatial orbitals can be characterized by either C or P .

(iii) Orthogonalisation of basis: Solving the Hartree-Fock

If the basis were orthogonal, S would be identity matrix; Hartree equation would become,

~~FC~~

$$FC = CE$$

which is just a usual matrix eigenvalue problem. ~~problem~~

Because of non-orthogonality, we need a way to solve the pseudoeigenvalue problem.

$$FC = SCE$$

This is done by orthogonalizing the basis functions.

We need to find a transformation matrix X such that

$$\phi'_\mu = \sum_\nu X_{\mu\nu} \phi_\nu, \quad \mu = 1, 2, \dots, k$$

form an orthonormal set

$$\text{i.e. } \int dr \phi'_{\mu}(r) \phi'_{\nu}(r) = \delta_{\mu\nu}$$

$$\int dr \phi_p^*(r) \phi_q(r) = \int dr \left[\sum_{\lambda} X_{\lambda p}^* \phi_{\lambda}^*(r) \right] \left[\sum_{\lambda} X_{\lambda q} \phi_{\lambda}(r) \right]$$

$$= \sum_{\lambda} \sum_{\mu} X_{\lambda p}^* \int dr \phi_{\lambda}^*(r) \phi_{\lambda}(r) X_{\lambda q}$$

$$= \sum_{\lambda} \sum_{\mu} X_{\lambda p}^* S_{\lambda \lambda} X_{\lambda q} = S_{pq}$$

* or $X^T S X = I$

Since S is Hermitian, it can be diagonalised by a unitary matrix U

$$U^T S U = D$$

where D is diagonal matrix of eigenvalues of S .

There are two common ways of orthogonalising the basis set.

(i) Symmetric orthogonalisation:

$$X = S^{1/2} = U D^{1/2} U^T$$

This leads to problem for basis sets with linear dependence & hence is not used.

(ii) Canonical orthogonalisation:

$$X = U D^{-1/2}$$

i.e. columns of V are divided by the square root of the corresponding eigenvalue.

Now, we can eliminate columns corresponding to eigenvalues equal to zero and convert the problem in symmetric orthogonalisation.

Now, consider $C' = X^T C \Rightarrow C = XC'$

$$FC = SCe$$

becomes, $F X C' = S X C'e$

Multiplying by X^+ on the left, we get

$$(X^T F X) C' = (X^T S X) C'e$$

define $F' = X^T F X$

, and use

$$\underbrace{F' C'}_{\downarrow} = C'e$$

These are the transformed Radon equations.

These can be solved by diagonalizing F' .
Once C' is obtained, C can be calculated.

(VII) The soft forest field prediction procedure

- 1) Specify atom + basis set.
- 2) Calculate overlap matrix S . Diagonalize it to get transformation matrix X .
- 3) Express coefft. matrix C as density matrix P .
- 4) Calculate E, P_1 .
- 5) Diagonalize F' to obtain C' .
- 6) Calculate C and density matrix P .
- 7) Compare P with old P . If converged, continue. If not return to step 4.
- 8) Use result as solution C to calculate any quantity of interest.

the density matrices can be compared by calculating standard deviation of successive density matrix elements

(iv) Expression for total energy

$$\text{E}_0 = 2 \sum_a^{N_1} h_{aa} + \sum_a \sum_b^{N_2} 2 J_{ab} - k_{ab}$$

from

$$= \sum_a^{N_2} h_{aa} (\text{h}_{aa} + \text{f}_{aa})$$

Substituting basis function expansion, we get

$$\text{E}_0 = \frac{1}{2} \sum_p \sum_v P_{pv} (\text{h}_{pv} + F_{pv})$$

Chapter 2

Kinetically balanced geometric Gaussian Basis set expression.

(i) Basis

In central field approximation,
in the ~~central field approximation~~, the solution to the Dirac equation is given by four component spinors:

$$\Psi_{nk\sigma}(r, \theta, \phi) = r^{\frac{1}{2}} \begin{pmatrix} P_{nk}(r) & X_{km}(0, \phi) \\ iQ_{nk}(r) & Y_{-km}(0, \phi) \end{pmatrix}$$

where P and Q are large and small component of ψ .

(ii) Matrix expression

Chapter - 3

Code

- i) Input parameters
- ii) Grid
- iii) Setting up
- iv) SCF procedure

Chapter - 4

Problems & Suggested solutions

Appendix Code