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Interaction of Electron with its Own Electric Field

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Interaction of electron with its own electric field is included in the Hartree-Fock-Roothaan theory. Coulomb integrals were calculated by interacting the charge density probabilities of all electrons in two volume elements of space and then it is extended over all space. Helium electronic ground state is studied by the use of the double zeta and panta zeta Slater-type orbitals as a basis set of functions. Imperical internal electronic coupling constant ξ, is introduced and its negative value indicate that interaction with self electric field is a kind of attractive (cohesion) force.

Key Words: Interaction, Electron, Electric, Field.

INTRODUCTION

Quantum mechanical studies of many electronic atoms are very complex. Because of the interelectronic repulsive interactions in electronic Hamiltonian, Eq (1), their Schrodinger equations have no exact solutions. Electronic Hamiltonian of an atom in the absence of relativistic interactions is[1–9]

$$\hat{H} = \Sigma_i \hat{H}_i + e'^2 \Sigma_{i>j} r_{ij}^{-1} \tag{1}$$

where $\hat{H}_i$, hydrogen like electronic Hamiltonian, is given by

$$\hat{H}_i = -(\hbar^2/2m_e)\,\hat{\nabla}_i^2 - ze'r_i^{-1} \tag{2}$$

and also z, $e' = e/(4\pi\varepsilon_0)^{1/2}$, m_e and $\hbar$ are the nuclear charge, electron charge in SI units, electron mass and the Plancks constant divided by 2π, respectively. Subsituting Eq. (2) in the Schrodinger equation yields wavefunctions, which are called "atomic spatial orbitals; AOs". Spin-orbital functions are built by combining such AOs with spin functions α and β. Atomic wavefunctions are constracted in terms of these functions, *e.g.*, Slater determinants, and frequently used in quantum mechanical calculations.

In the Hartree and the Hartree-Fock methods, interelectronic repulsive interactions, second term in Eq. (1) are calculated by considering that every electron is moving in the electric field of remaining electrons. The difference between these methods lies in the indistinguishability principle of electrons of an atom and the exchange integrals. In the Hartree method, atomic wavefunctions are written as a product of single electron wavefunctions such as:

$$\psi = \Pi_i \psi_i \qquad \ldots (3)$$

Orthonormal spin wavefunctions have no role in calculations and ψ_i of Eq. (3) are only the spatial part of the spin-orbitals. If the Schrodinger equation is solved for energy we obtain:

$$E = \Sigma_i < \psi_i | \hat{H}_i | \psi_i > + e'^2 \Sigma_i < \psi_i | \Sigma_{j=i+1} < \psi_j | r_{ij}^{-1} | \psi_j > | \psi_i > \qquad (4)$$

Calculations are carried out by using central field approximation and self consistent field (SCF) theory, either by numerical AO's of Hartree technique[10], or Roothaan adapted method[11]

For the following resons it is needed to include the interaction of electrons with their self electric field of many electronic atoms in the Hartree-Fock calculations.

1. Hartree model in the other view: An atom with no external interaction is a steady system and quantum mechanics requires that the atom must be in a stationary (ground) state. Denoting the marked electron by i and all others by j at the moment t, and with the illustration of Fig. 1 we have charge density probabilities of electron i in the volume element

$$B = e' |\psi_i(B)|^2 \, dv_i$$

Sum of charge density probabilities of electrons j in the volume element

$$A = e' \, \Sigma_{j \neq i} |\psi_i(A)|^2 \, dv_j.$$

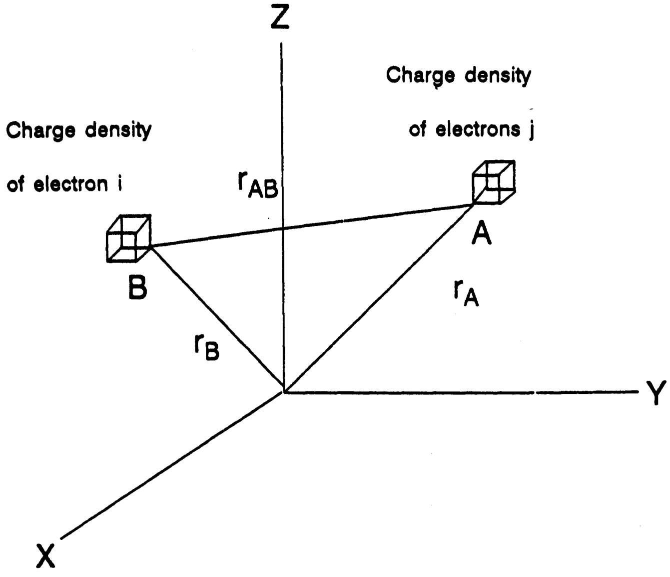

Fig. 1. Hartree presentation of an atom

It should be mentioned that repulsion between electrons j in volume element A is not taken into the account and charge density probabilities are considered additive quantities.

Let two charge densities in A and B to interact with each other, then repulsion between electron i in B and electrons j in A is given by:

$$(e'|\psi_i(B)|^2)r_{AB}^{-1}(e' \Sigma_{j=i}|\psi(A)|^2 dv_j)$$

(ejection), it is considered that the electron interacts with its electric field[12, 13]. In expansion of perturbation sery of energy surfaces of electrons figures are generated. One of which is the correction term for self interaction of the electron with its own field, which is presented in Fig. 2.

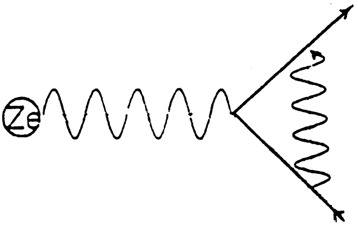

Fig. 2. The electron emits an imaginary photon, then exchanging a photon with the nucleus, it absorbs the emitted imaginary photon

Self interaction is not limited to the quantum electrodynamics and it could happen in the same way in unrelativistic quantum mechanics.

3. The coulombic self interactions are cancelled out by opposite sign of the coresponding self exchange interactions[2]. Because of spin orthogonality there is no exchange integral in He atom. In present view self interaction can only be in Coulombic form.

The Model: At the time t, let charge density probability distribution of all electrons in atomic space to settle down. The sum of charge electron i can be in any existing electron in the atom so, repulsion of charge densities of electrons between two volume elements is given by

$$(e' \Sigma_i |\psi_i(B)|^2 dv_i)r_{AB}^{-1}(e' \Sigma_{j=i+1} |\psi_j(A)|^2 dv_j)$$

In order to avoid repeating counting of interaction between electrons i and j the index of second sum is changed from $j \neq i$ to $j = i + 1$. The interaction must be smeared all over the space, therefore repulsion between electrons is being

$$\iint_{\text{all space}} e'^2 \Sigma_i |\psi_i|^2 dv_i r_{ij}^{-1} \Sigma_{j=i+1} |\psi_i|^2 dv_j \tag{5}$$

which is the same as the second term of Eq. (4).

Charge density probabilities in volume elements being an additive quantities. Coulomb law have no restrictions on interaction of two parts of charge densites of two different electrons and nor on two different parts of the same electron. Electrons of an atom are not distinguishable and have the same nature. Labling electrons by i and j must not be reason to exclude charge density probability of electron i from volume element B. So there is no reason for having no interaction between two parts of the charge density probabilities of one electron at time t.

Also, it is not in contradiction with the undiviceblity principle of the electron. Self Coulombic interaction is called "Internal Coupling" and needed to be taken into account.

2. Quantum Electrodynamics: In explaning electron wobling density probabilities in two volume elements A and B, Fig. (1), interact each other and covers all the space. Coulomb integrals are given by

$$\text{Coulomb integrals} = e'^2 \iint_{\text{all space}} (\Sigma_i |\psi_i|^2 dv_i) r_{ij}^{-1} (\Sigma_{j=i+1} |\psi_j|^2 dv_j)$$

$$+ e'^2 \iint_{\text{all space}} (\Sigma_i \xi_i |\psi_i|^2 dv_i) r_{ii}^{-1} (|\psi_i|^2 dv_i) \tag{6}$$

where the first term is the repulsion between different electrons and the second term in Eq. (7) is the interaction of the electron with its own electric field; internal coupling. Supposing the interaction is taken between two one half of an electron, ξ will have a value of 0.25, however its value will be determined latter.

For illustration, the He atom ground state is considered. The atomic wavefunction, ϕ (1, 2), is taken a single Slater determinant. The ground state energy of the He atom is given by:

$$E = 2\langle \phi_{1s}(1) | H_1 | \phi_{1s}(1) \rangle + (1 + 2\xi) \langle \phi_{1s}(1) \phi_{1s}(2) | r_{12}^{-1} | \phi_{1s}(1) \phi_{1s}(2) \rangle \tag{7}$$

In Hartree-Fock-Roothaan (HFR) method[11, 14] spin orbitals are represented by a linear combination of an appropriated set of basis functions such as:

$$\phi_i = \Sigma_\mu^{N'} c_{i\mu} \chi_\mu \tag{8}$$

where χ_μ is a basis function and usually taken Slater type orbitals (STO) or Gaussian type orbitals (GTO), $c_{i\mu}$ is the μth expansion coefficients of spin orbital. Double zeta Slater orbitals (DZ-STO)[11] and Panta zeta-STO, (PZ-STO)[8] with fixed exponents are used and only expansion coefficients are optimized. In matrix notation HFR equation are:

$$H_R^F C = SC\varepsilon \tag{9}$$

where

$$H_R^F = H + G \tag{10}$$

and matrix elements are

$$H_{kl} = \langle \chi_k | H | \chi_l \rangle$$

$$G_{kl} = (1 + \xi)\, \Sigma_{rs} \langle kl | r_{ij}^{-1} | rs \rangle R_{rs}$$

$$S_{kl} = \langle \chi_k | \chi_l \rangle$$

$$\varepsilon_i = -\text{Ionization potential}$$

$$R = CC^\dagger$$

Basis functions are orthonormalized using symmetry orthogonalization method and the Jacobi method is used to diagonalize[15] matrices. Results of calculations are summized in Table-1 for DZ-STO and in Table-2 for PZ-STO.

TABLE-1

COMPARISON OF He GROUND STATE VARIABLES (DOUBLE ZETA STO)

Variable	DZ-STO(a)	DZ-STO(b)	DZ-STO(c)	Expt.
E	–2.86167H –77.85 eV	–2.86167H –77.87 eV	–2.90320H –79.00 eV	–2.9032H –79.0 eV
IP	0.91794H	0.917935H	0.95706H	
ζ_1	3.0	2.91093	2.91093	
ζ_2	1.4	1.45363	1.45363	
C_1	0.884315	0.843784	0.837703	
C_2	0.175261	0.180687	0.187494	
ξ	0	0	–0.040390	

(a) ref. 14; (b) ref. 11; (c) present work.

TABLE-2

COMPARISION OF He GROUND STATE VARIABLES (PANTA-ZETA STO)

Quantity	PZ-STO(a)	PZ-STO(b)	Exptl.
E	–2.86168H –77.870 eV	–2.903205H –79.000 eV	–79.0 eV
IP	0.917948H	0.955190H	
C_1	0.76838	0.743851	
C_2	0.22346	0.259899	
C_3	0.04082	0.017464	
C_4	–0.00994	0.008505	
C_5	0.00230	–0.005274	
ξ	0	–0.040310	

$\zeta_1 = 1.41714$ $\zeta_2 = 2.37682$ $\zeta_3 = 4.39628$
$\zeta_4 = 6.52699$ $\zeta_5 = 0.008505$ ζ values for both
cases are the same (a) ref. 8 (b) present work.

Conclusion

Table 1 and 2 show a negative value for ξ, which indicate the interaction of an electron with self electrical field is an attraction. Therefore, self interaction can be considered as a kind of cohesion force and the electron has more solidity than other related methods.

In the present model one extra parameter for each spin orbital will be fixed. In the absence of ξ for He ground state 4 parameters in DZ-STO and 10 parameters in PZ-STO needed to be fixed. Comparing DZ-STO and PZ-STO a little improvement in energy value is observed. The energy values for $\xi = 0$ to be compared in Tables 1 and 2. Actually N′ of Eq. (8) must be very large and for each spin orbitals a huge number of parameters to be fixed. An increase of one parameter is not complicating the calculations too much. The difference in ξ values of DZ-STO and PZ-STO appears in fifth digit of decimal point therefore using this method with low values of N′ can yield an acceptible result with saving time.

Ionization energy with respect to other methods increase about 4.5% which can be interpretated due to internal coupling and because of that, electron a little more strongly binded to the nucleous.

Finally, by adjusting ξ value the experimental values of energy can be determined with high accuracy (Tables 1 and 2).

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