NOVOSADOV'S METHOD OF MOLECULAR HARMONICS RESEARCH FOR QUANTUM MECHANICS COMPUTER MODELING

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Abstract – Analytical solving of single-electron Schrödinger equation in Columb multi-nuclear field proposed by Novosadov results with molecular orbitals represented as linear sum of hydrogen like orbitals centered in atom cores. Author research a possibility of Novosadovs method application for modeling of atoms and molecular systems. Results of calculations of H2+ electron density and interaction energy dependence on distance for H-H, C-C and metan- ch4 are represented.

I. INTRODUCTION

For solutions of the Schrödinger equation, various approximate methods including Self Consistent Field and Density Functional Theory are using. To construct the wave function Gaussian orbitals are used, which are poorly reproduce the electron density distribution in atoms and molecules and have the wrong asymptotic behavior at a distance from the nucleus. Novosadov proposed methods of construction and algorithms for computing multi-center matrix elements in the basis of atomic orbitals with the exponential asymptotic behavior, which include Slater hydrogen-like functions, and Bessel functions. Developed algorithms are universal for all orbital types are numerically stable and allows to achieve any accuracy.

II. SINGLE-ELECTRON SCHRÖDINGER EQUATION SOLVING

For solving problem of one electron moving in the fixed nuclei field Shcrodinger equation could be represented as

$$\left(\frac{1}{2} p^2 - \sum_{\alpha=1}^{N} Z_\alpha r_\alpha^{-1} \right) \psi = E\psi \tag{1}$$

where $r_\alpha = \left| \vec{r} - \vec{R}_\alpha \right|$, $\vec{r}$, $\vec{R}_\alpha$ - electron and α- nuclei coordinates correspondingly.

In the electron pulse space equation (1) is represented as integral equation:

$$\frac{1}{2} p^2 \psi(p) - \frac{1}{2\pi^2} \sum_{\alpha=1}^{N} \int Z \exp[i(\vec{p} - \vec{p}')\vec{R}_\alpha](\vec{p} - \vec{p}')^{-2} \psi(\vec{p}') d^3\vec{p}' = E\psi\vec{p}) \tag{2}$$

Equation (2) can be transformed to angle pulse variable by stereographic projection on the Riemann sphere:

$$p_0 \tau(\alpha) \psi(\alpha, \theta, \ ) = (2\pi^2)^{-1} \int Z(\vec{p}, \vec{p}')[4\sin^2(\omega/2)]^{-1} \Psi(\alpha', \theta', \ ') d\Omega_4' \tag{3}$$

After applying bilinear expansion

$$[4\sin^2(\omega/2)]^{-1} = \sum_{n=1}^{\infty} \sum_{l=0}^{n-1} \sum_{m=-l}^{l} n^{-1} \Psi_{nlm}(\Omega_4) \Psi_{nlm}(\Omega_4') \tag{4}$$

eq. (3) leads to matrix equation

$$Tc - p_0 Ic = 0, (5), \text{ where } p_0 = (2|E|)^{1/2}$$

Finally, discrete electron specter solving reduced to matrix equation

$$A(p_0\,)\vec{c} - p_0 I \vec{c} = 0 \tag{6}$$

Elements of matrix A are calculated as

$$A_{\alpha n l m}^{\alpha' n' l' m'} = [\,Z_\alpha Z_{\varepsilon'}(nn'\,)^{-1}\,]^{1/2}\,S_{nlm}^{n'l'm'}(\vec{R}_{\alpha\alpha'}\,), \tag{7}$$

$$S_{\alpha n l m}^{\alpha' n' l' m'} = \sum_{NLM} \pi^{1/2}\,p_0^{-3/2}\,u_{NLM}(\vec{R}_{\alpha\alpha'})\,JT(n'\,l'\,m',nlm;\,NLM)\,, \tag{8}$$

$$T(n'\,l'\,m',nlm;\,NLM) = (\,2\pi^2\,)^{-1}\int 4\mathrm{p}_0^2(p_0^2 + p^2\,)^{-1}\psi_{n'l'm'}(\Omega\Omega)_{nlm}(\Omega\Omega)_{NLM}(\Omega\Omega)d \tag{9}$$

Where $u_{NLM}(\vec{R})$ - hydrogen like orbital, and R_{aa} – distance between Ra and Ra atoms centers.

Fixing parametr p0 in the matrix elements we can find specter p0i(p0). Points where the curves p0i(p0) cross line y=p0 corresponds solving of eq. (6) and consequently eq. (3).

When parameter p0 and eigvectors are found wave function can be introduced as

$$\Psi(r) = p_0^{-1}\sum_{\alpha=1}^{N}\sum_{nlm}(Z_\alpha/n)^{1/2}c_{\alpha nlm}u_{nlm}^{*}(r - R_a\,) \tag{9}$$

Where c_{alnm} is a_{lnm} element of eigenvector c and

$$N \in [\,|n - n'| + 1, n + n' - 1\,], \quad L \in [\,|l - l'|, l + l'\,], \quad M = m - m'; \quad N > L, \quad L \geq |M|$$

III. ATOMIC SYSTEMS PROPERTY CALCULATIONS

On the figure 1 specter p0i(p0) calculated for the molecula H2+ and C2 are represented. Matrix A degree is reduced to 10x10 by setting maximum n to 2. According to figure 1 a) there are 4 solution for p0 . Others curves cross line y=p0 only in po=0.
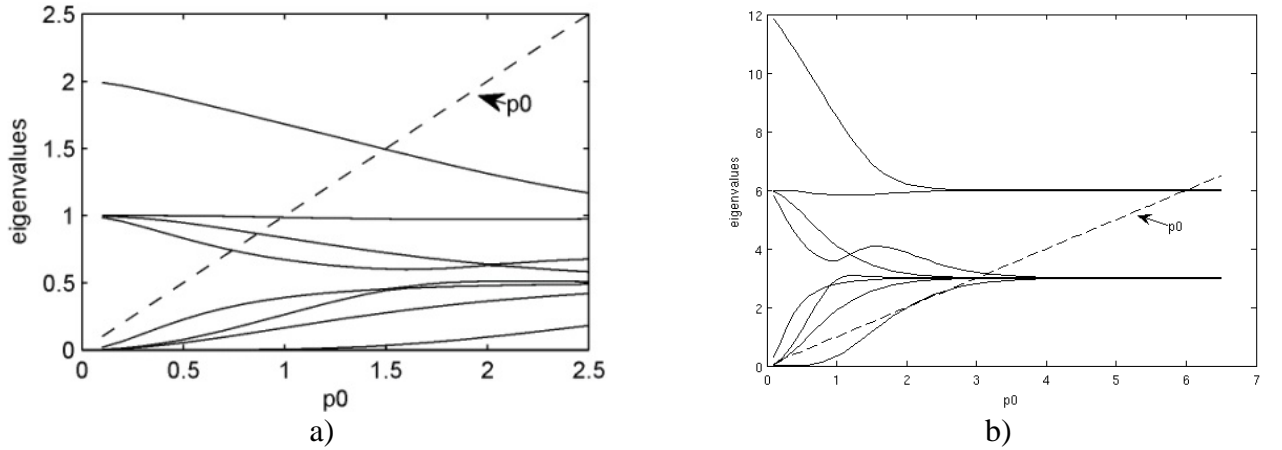

Figure 1 – p0i(p0) calculated for a) H2+ b) C2

On the figure 1 b there are 10 solutions for p0 corresponding to energies of ten orbitals formed from atom C orbitals and four additional solutions where curves cross the line y=p0 corresponding higher energies that may be caused by matrix reduction and not have physical sense.

The value of two lower wave functions square is calculated for the systems of two hydrogens atoms where distances between atoms are 1.7 and 5 a.u. (figure 2 a,b).
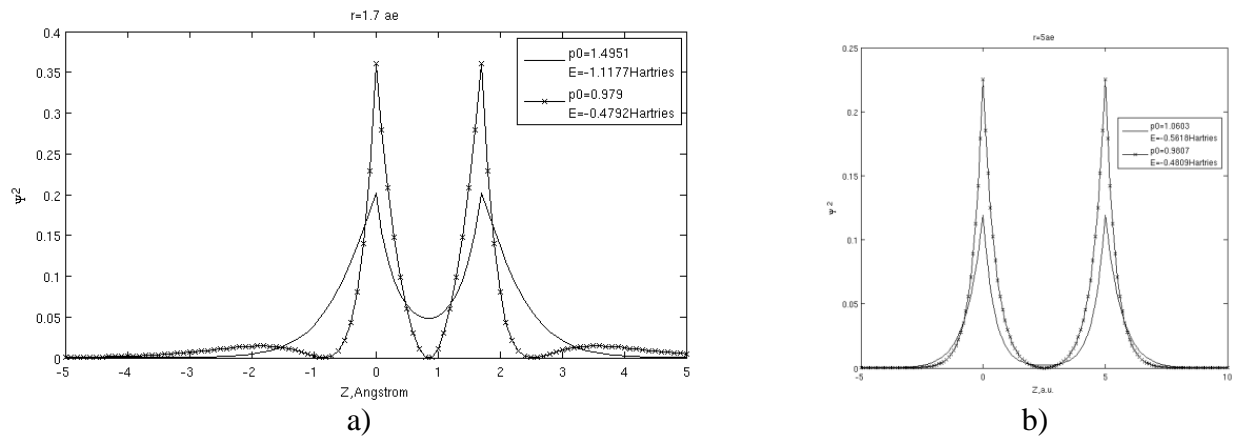
Figure 2 – Wave functions square calculated for the systems of two hydrogens atoms

Figures 2 a,b shows that molecula H2+ has binding and antibonding orbitals which trend to atomic orbitals when the distance between atoms increase. Calculation of one-electron energy dependence in field of two proton represented on figure 3 shows that the Matrix A reduced to n=1 is insufficient to correct calculation of electron state.

When the p0 is maximum of possible solutions all eigenvalues of matrix A are smaller than p0 and when the p0=0 all eigenvalues are biger. Therefore the number of solutions in the field more than some value can be calculated as the number of eigenvalues curves above the line y=p0 for p0=value when there are no more than one crossing with the line y=p0 for every curve.

III. CONCLUSION

Developed by the authors computer implementation of the method of molecular harmonics can solve the one-electron problem, which has important theoretical value in quantum chemistry. The calculated energies and the lower orbital wave functions of simple atomic structures are consistent with those of experimental and theoretical studies.

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