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Note

Application of the Screened Coulomb Potential to the Molecular System (H_2)

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The electronic correlation in atoms and molecules is the main problem of the *ab-initio* calculations. There are many methods that include the correlation between electrons[1].

In this work we would like to describe the electronic correlation from another point of view. In the many-body theory[2] the Coulomb potential becomes screened which means that instead of the long range potential one has to deal with a potential of finite range. With this idea in mind we applied a simple finite range potential to the molecular problem. We choose the potential of the form

$$V(1, 2) = \exp(-\alpha r_{12}) / r_{12} \qquad (1)$$

where r_{12} is the distance between two electrons and $D = 1/\alpha$ is the screening length. This is Yukawa potential which is applied in nuclear theory. Because this potential (1) is of finite range, the calculated properties of the system (ground state energy) can be below the measured ones depending on the value of α. α is chosen from the requirement that the calculated energy is equal to the experimental one. This parallels the empirical determination of parameters of the potential as *e. g.* in the pseudopotential method[3].

We applied the Yukawa potential to the molecule H_2. The employed Hamiltonian contained the kinetic part, the Coulomb potential between nucleus and electrons, the nuclear repulsion energy and the potential of the form (1) between two electrons. The trial wave function was in the LCAO form with 1s Slater atomic orbitals with variable exponent ξ. All integrals were calculated in analytical form except the exchange integral. Because of the limitations of the computer (Zuse-23) we were not able to evaluate numerically this integral. The ground state energy was calculated for various values of α; for each α a minimum was found in ξ (Table I values in atomic units).
The experimental energy of the H_2 molecule is obtained in the order of magnitude for α of about 0.2. A rough estimation from the many-body theory[2] gives the value near 1. The value of D is much larger than the range of the system. It is interesting to compare the molecular system with the atomic one (He). The ground state energy of He was calculated with the trial wave function of the form:

$$\psi(1,2) = 1s(1) \cdot 1s(2) \cdot [\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1)]$$

where 1s(i) is the Slater orbital with a variable exponent ξ and with interelectronic potential (1). As in the H_2 molecule the value $D = 5$ *a. u.* was obtained. This value is twice the diameter of the »Coulomb hole« (the range of the correlation[4]). We expect the same order of magnitude for the »Coulomb hole« in H_2.

TABLE I

Total Energy

ξ \ α	0.0	0.2	0.3	0.4
1	1.11425	1.17078	1.22666	1.27214
1.1	1.13644	1.19841	1.25761	1.30641
1.2	1.13607	1.20330	1.26561	1.31755
1.3	1.11396	1.18631	1.25157	1.30647

From the calculated value of D the following conclusion emerges: to obtain the main part of the correlation energy it is not sufficient to carry out the summation over just one sort of diagrams in Bruckner-Goldstone perturbation theory. This was confirmed by Kelly in the calculation of correlation energies of atom[5].

Recently it was shown that the RPA (Random-Phase-Approximation) can give valuable information for the correlation energy. In the many-body theory the potential (1) is obtained by using the RPA method in a model system[2]. It may be inferred from this that this potential can be used even for π electrons, thus introducing the screening by the nucleus and the σ parts. In the Pariser-Parr-Pople approximation this means that the two-center Coulomb integrals are given with $V(1, 2)$ instead of with $1/r_{12}$.

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IZVLEČEK

Uporaba zasenčenega Coulombskega potencijala na molekulskem sistemu (H_2)

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S uporabo enostavnega Yukawinega potencijala, smo pokazali, da je sumacija samo po eni vrsti diagramov Bruckner-Goldstone perturbacijske teorije nezadostna. Iz velikosti D sledi, da je »doseg korelacije« verjetno isti pri H_2 in He.

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