

Calculation of singlet and triplet energy states of the two-dimensional (2D) H^- ion and 2D He atom

Abstract

Singlet and triplet energy states of the two-dimensional (2D) H^- and 2D He ions were calculated. A multi parameter system of Gaussian orbitals with exponentially correlated multipliers is used. An analog of the H^- ion is a two-electron shallow D^- center in covalent semiconductors. The energy of the lowest triplet term of 2D D^- center coincides with the bottom of the conduction band, which is a numerical illustration of Hill's theorem of the existence the only bound state for the hydrogen anion. The ground state energies and variational parameters for test wave functions are obtained. Useful limiting transition to the case of complete screening of the Coulomb repulsion V_{ee} has been investigated. In this case, the Hamiltonian 2D H^- transforms into a two-dimensional hydrogen-like atom with two noninteracting electrons. The distribution of electrons by energy levels is carried out according to the Pauli principle. In a singlet state, the energy of such atom corresponds to the doubled ground state energy, in triplet one it is the sum of the energies of the ground and first excited states of the 2D hydrogen atom. The results are compared with the calculations performed by other authors. The energies obtained in the work with the use of Gaussian orbitals are the lowest in comparison with the results that have already been calculated by other authors for Slater type orbitals. This indicates a high accuracy of calculations with using Gaussian orbitals.

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Abbreviations: 1D, one-dimensional; 2D, two-dimensional; 3D, three-dimensional; MOC, metal oxide compounds; HTSC, high-temperature superconductivity

Introduction

Atoms and molecules with a reduced dimension can arise in large external magnetic fields. The magnetic traps were used by Görlitz et al¹ in order to transfer sodium atoms to lower dimensional states. Transitions of sodium atoms in both two-dimensional (2D) and one-dimensional (1D) state were realized. Super strong magnetic fields can occur in the plasma of the Sun and stars. Therefore, in principle, one can observe the spectra of two-dimensional atoms and molecules in them. As is well known, on the Sun and Sun-like stars, the atoms of hydrogen and Helium lead to a small absorption of light. The main absorption provides a negative hydrogenion.² Metal atoms make a small contribution to absorption, since their number is tens of thousands of times smaller than those of hydrogen atoms. Such a negative ion is formed when a second electron is attached to a hydrogen atom. The numerical research of anisotropic characteristics of a two-dimensional (2D) hydrogen atom induced by a magnetic field was carried out for Koval et al.³ Under terrestrial conditions, H^- ions are unstable due to their extremely high chemical activity. A complete analog of the H^- in semiconductor crystals is the D^- center with a negative charge, i.e. a shallow hydrogen-like donor center that has captured an additional electron. The development of nanotechnologies has led to the emergence of new materials, such as two-dimensional monoatomic layers of various compositions. Graphene is a well-known example of a crystal with a two-dimensional_hexagonal lattice in which one atom forms each vertex. There are other materials with a structure

close to graphene.^{4,5} In such materials, it is possible to observe two-dimensional analogues of D^- centers in three-dimensional

(3D) systems, as well as neutral two-electron states, similar to the He atoms.

Examples of two-dimensional systems are crystal structures that have translational symmetry in only two directions. Two-dimensional crystals can be located on the surface of bulk crystals, or on the surface of liquid solutions. Conductive layers in cuprate metal oxide compounds (MOC), in which high-temperature superconductivity (HTSC) was observed, can be considered as two-dimensional systems. Two-dimensional crystals have a band structure and can be both metals and semiconductors or dielectrics. Variational methods are used in the problems of quantum physics and chemistry devoted to the calculations of the energy spectrum of atomic and molecular systems. The energy functional of two-electron systems for 2D H^- and 2D He was obtained analytically using a Gaussian basis with exponentially correlated multipliers. Variational calculations were performed by random search methods and Hook-Jeeves method. The reasons why the random search method is preferred for optimization problems with a large number of parameters are described in review article.⁶ Hook-Jeeves method was used at the final stage to improve the accuracy of variational calculations.⁷

Basic formulas and relations

1. Let's first look at a single-electron 2D atom. In atomic units (at. un.) ($m=1$, $e=1$, $\hbar=1$), the Hamiltonian of a two dimensional atom with one electron has the form:

$$H_1 = -\frac{\Delta_1}{2} - \frac{Z}{r_1} \quad (1)$$

where, Z is the charge of the nucleus, the subscript 1 is introduced to denote a single-electron system, Δ_1 – is the Laplace operator in a two-dimensional system:

$$\Delta_1 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2},$$

two-dimensional radius-vector is determined by the expressions:

$$\mathbf{r}_1 = \mathbf{i}x_1 + \mathbf{j}y_1, \quad r_1 = \sqrt{x_1^2 + y_1^2}$$

here \mathbf{i}, \mathbf{j} – are the directing unit vectors in two-dimensional space.

The trial variational function is selected in the form:

$$\Psi_1 = \sum_{i=1}^n C_i \exp(-a_{1i} \cdot r_1^2), \quad (2)$$

where c_i, a_{1i} are the variational parameters, $a_{1i} > 0, i = 1, \bar{n}$.

We introduce simplifying notation for the squared wave function (WF):

$$\Psi_1^2(r_1) = \sum_{i=1}^n \sum_{j=1}^n c_i c_j \exp(-\alpha_{ij} r_1^2)$$

where $\alpha_{ij} = a_{1i} + a_{1j}$.

Normalization integral is:

$$N_1 = \int \Psi_1^2(r_1) d\sigma_1,$$

where $d\sigma_1 = dx_1 dy_1$ is the element of the area in two-dimensional space.

Integration is performed in infinite limits in Cartesian coordinates:

$$\int \{...\} d\sigma_1 = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \{...\} dx_1 dy_1.$$

$$\Psi_{12}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i=1}^{n_0} c_i (1 + (-1)^S \mathbf{P}_{12}) \exp(-a_{1i} r_1^2 - 2a_{2i}(\mathbf{r}_1 \cdot \mathbf{r}_2) - a_{3i} r_2^2) \quad (4)$$

where \mathbf{P}_{12} is the operator of permutation of electron coordinates, $S=0$ for the singlet state, $S=1$ for the triplet state; $\mathbf{r}_1, \mathbf{r}_2$ are the radius vectors of the first and second electrons, respectively, $c_i, a_{1i}, a_{2i}, a_{3i}$ are the variational parameters ($a_{1i}, a_{3i} > 0$).

To simplify the calculations, the automatic WF symmetrization procedure is introduced. Always choose even $n=2n_0$. For $i > n_0$ we assume:

$$a_{1i} = a_{3(i-n_0)}, \quad a_{2i} = a_{2(i-n_0)}, \quad a_{3i} = a_{1(i-n_0)}.$$

For singlet states, we assume $C_i = C_{i-n_0}$, for triplet states $C_i = -C_{i-n_0}$.

Taking into account the automatic symmetrization of the WF, we omit the factor $(1+(-1)^S \mathbf{P}_{12})$ and rewrite the two-electron WF in the form:

$$N_1 = \pi \sum_{i,j=1}^n c_i c_j \alpha_j^{-1}$$

Kinetic energy is:

$$T_1 = \frac{1}{2} \int |\nabla \Psi_1|^2 d\sigma_1,$$

$$T_1 = 2\pi \sum_{i,j=1}^n c_i c_j \frac{a_{1i} a_{1j}}{\alpha_j^2}$$

For potential energy we get:

$$V_{1q} = -Z \int \frac{\Psi_1^2(\mathbf{r}_1)}{r_1} d\sigma_1,$$

$$V_{1q} = -Z\pi\sqrt{\pi} \sum_{i,j=1}^n \frac{c_i c_j}{\sqrt{\alpha_{ij}}}$$

The energy of the ground state of a single-electron 2D atom has the form:

$$E_1 = \min_{\Psi_1} \left(\frac{T_1 + V_{1q}}{N_1} \right)$$

2. Hamiltonian of two-electron 2D atoms has the form

$$3. \quad H_2 = -\frac{\Delta_1}{2} - \frac{\Delta_2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}, \quad (3)$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$

The variational functions of the singlet and triplet states of two-electron atoms are chosen in the form:

$$\Psi_{12}(r_1, r_2) = \sum_{i=1}^n c_i \exp(-a_{1i} r_1^2 - 2a_{2i}(\mathbf{r}_1 \cdot \mathbf{r}_2) - a_{3i} r_2^2). \quad (5)$$

We introduce simplifying notation for the squared wave function:

$$\Psi_{12}^2(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i=1}^n \sum_{j=1}^n c_i c_j \exp(-\alpha_{ij} r_1^2 - 2\beta_{ij}(\mathbf{r}_1 \cdot \mathbf{r}_2) - \gamma_{ij} r_2^2)$$

where

$$\alpha_{ij} = a_{1i} + a_{1j}, \quad \beta_{ij} = a_{2i} + a_{2j}, \quad \gamma_{ij} = a_{3i} + a_{3j},$$

$$\alpha_{ij} > 0, \quad \gamma_{ij} > 0.$$

Normalization integral:

$$N_2 = \int \Psi^2(r_1, r_2) d\sigma_{12}$$

where $d\sigma_{12} = dr_1 dr_2$.

$$N_2 = \pi^2 \sum_{i,j=1}^n c_i c_j \zeta_{ij}^{-1}$$

$$T_2 = 2\pi^2 \sum_{i,j=1}^n c_i c_j \zeta_j^{-2} \left[\alpha_j (a_{2i} a_{2j} + a_{3i} a_{3j}) + \gamma_j (a_{1i} a_{1j} + a_{2i} a_{2j}) - \beta_{ij} (a_{1i} a_{2j} + a_{2i} a_{1j} + a_{3i} a_{2j} + a_{2i} a_{3j}) \right]$$

In order to calculate the potential energy, it is convenient to introduce the following Fourier components of the two-electron wave function:

$$W_{12q} = \int \Psi_{12}^2 \exp(i\mathbf{q}\mathbf{r}_{12}) d\sigma_{12},$$

$$W_{1q} = \int \Psi_{12}^2 \exp(i\mathbf{q}\mathbf{r}_1) d\sigma_{12},$$

$$W_{2q} = \int \Psi_{12}^2 \exp(i\mathbf{q}\mathbf{r}_2) d\sigma_{12},$$

where $\Psi_{12} \equiv \Psi_{12}(\mathbf{r}_1, \mathbf{r}_2)$, $\mathbf{q} = \mathbf{i}q_x + \mathbf{j}q_y$, is two-dimensional vector.

Calculating the Fourier components in the Cartesian coordinate system, we obtain:

$$W_{12q} = \pi^2 \sum_{i=1}^n c_i c_j \zeta_{ij}^{-1} \exp(-q_{12ij} q^2),$$

$$W_{1q} = \pi^2 \sum_{i=1}^n c_i c_j \zeta_{ij}^{-1} \exp(-q_{1ij} q^2),$$

$$W_{2q} = \pi^2 \sum_{i=1}^n c_i c_j \zeta_{ij}^{-1} \exp(-q_{2ij} q^2)$$

$$V_{2q} = \pi^2 \sqrt{\pi} \sum_{i,j=1}^n c_i c_j \frac{1}{\sqrt{\zeta_{ij}}} \left(\frac{1}{\sqrt{\alpha_{ij} + 2\beta_{ij} + \gamma_{ij}}} - Z \left(\frac{1}{\sqrt{\alpha_{ij}}} + \frac{1}{\sqrt{\gamma_{ij}}} \right) \right)$$

The energy of a two-electron system in 2D space is determined by the expression:

$$E_2 = \min_{\Psi_{12}} \left(\frac{T_2 + V_{2q}}{N_2} \right)$$

Results of variational calculations

Variation calculations were performed by random search methods and the Hook-Jeeves method. For a multiparameter system, the method of random search is the most accepted, because it does not lead to a long-term hang of the program associated with the search for

where $\zeta_{ij} = \alpha_{ij} \gamma_{ij} - \beta_{ij}^2$, $\zeta_{ij} > 0$.

Kinetic energy is:

$$T_2 = \frac{1}{2} \int (|\nabla_1 \Psi_{12}|^2 + |\nabla_2 \Psi_{12}|^2) d\sigma_{12},$$

where $q_{12ij} = 0.25 \zeta_{ij}^{-1} (\alpha_{ij} + 2\beta_{ij} + \gamma_{ij})$,

$q_{1ij} = 0.25 \zeta_{ij}^{-1} \gamma_{ij}$, $q_{2ij} = 0.25 \zeta_{ij}^{-1} \alpha_{ij}$.

To calculate the integral expressions in potential energy, we use the relations:

$$\int \frac{\Psi_{12}^2}{r_{12}} d\sigma_{12} = \int \frac{W_{12q}}{2\pi q} d\mathbf{q},$$

$$\int \frac{\Psi_{12}^2}{r_1} d\sigma_{12} = \int \frac{W_{1q}}{2\pi q} d\mathbf{q},$$

$$\int \frac{\Psi_{12}^2}{r_2} d\sigma_{12} = \int \frac{W_{2q}}{2\pi q} d\mathbf{q}.$$

Calculating the integrals over the wave vector in the polar coordinate system, we obtain for the Coulomb part of the energy functional of two-electron systems in 2D space:

$$V_{2q} = \int \left(\frac{1}{r_{12}} - Z \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \right) \Psi_{12}^2(\mathbf{r}_1, \mathbf{r}_2) d\sigma_{12},$$

a minimum of other methods. However, to increase the accuracy of the calculations, we used both methods. Table shows the results of the variational calculations of the energies of the negative 2D hydrogen ion and 2D helium atom in the singlet and triplet state. The calculated energy values are obtained for 30 independent exponents ($n_0=30$) in the WF.⁴ The zero energy of the triplet term illustrates, that in the absence of a magnetic field, the 2D ion H⁻ has a single bound state that corresponds to the singlet term just like 3D ion H⁻.¹¹ For the D-center, the energy of the exchange interaction, which can be defined as the difference between the energies of the singlet and the lowest triplet states, is exactly equal to the energy of the ground state. As can be seen from Table 1, for the triplet state of 2D H⁻, the energy of the Coulomb repulsion of electrons tends to zero. With a further increase

in the number of exponents in the WF (4), this assumption can be verified numerically. We can obtain the useful boundary transitions from the two-electron system to the 2D H by equating to zero the last term in the Hamiltonian (1), corresponding to the interelectron repulsion. After performing variational calculations, we obtain for the case $V_{ee} = 0$ (where V_{ee} is the energy of interelectron interaction): in the singlet state, the energy H⁻ is equal to twice the energy of a two-dimensional hydrogen atom, which in atomic units is -3.999999. In the triplet state, the energy calculated by us is equal to -2.222219

at. un. The value of the energy of the triplet term obtained by us corresponds to the exact value of the total energy of the ground (-2.0 at. un.) and the first excited state (-0.2 at. un.) of a 2D hydrogen atom.² This example is a numerical illustration of the Pauli principle. Thus, electrons with opposite spins occupy the ground state, and when the spins are the same, one of the electrons necessarily passes into the next orbital with higher energy. For comparison, we present the value of the ground state energy of a two-dimensional hydrogen atom $E_1 = -0.999995$, obtained using the one-electron WF (2) for $n = 14$.

Table 1 Total energy of singlet (S=0) and triplet (S=1) terms E_2 (in at. un.) and various contributions to the energy of a 2D H⁻ (Z=1) and 2D He (Z=2) atoms: T is kinetic energy, E_{ext} is the total energy of electron interaction with the nucleus, V_{ee} is the electron repulsion energy, V_{ee}^{3D} is the energy of the interelectron repulsion for 3D atoms

S	Z	E_2	E_2 [8]	E_2 [9]	E_2 [10]	T	E_{ext}	V_{ee}	V_{ee}^{3D}
0	1	-2.23938	-2.2338	-1.996	-1.96	2.239764	-5.66106	1.181455	0.3146
1		-1.99998	-	-	-	1.999978	-4.00139	0.001435	0
0	2	-11.8981	-11.8881	-11.6472	-11.56	11.8978	-27.3029	3.507033	0.9487
						11.8904 ^[8]	-27.2769 ^[8]	3.4985 ^[8]	
1		-8.2816	-	-8.22	-	8.2718	-17.029	0.4753	-

Discussion

This research presents an example of variational calculation of energies for two-electron atomic systems in two dimensions using Gaussian functions with correlation factors. The energy functional of two-electron 2D systems is presented in an analytical form and

$$\Psi_2^{2D}(r_1, r_2, r_{12}) = C_N \exp(-2Zr_1) \exp(-2Zr_2) f_1(a, r_1, r_2) f_2(b, r_{12}), \quad (6)$$

where C_N – normalization factor, a, b – variational parameters;

$$f_1(a, r_1, r_2) = \cosh(ar_1) + \cosh(ar_2)$$

$$f_2(b, r_{12}) = 1 + r_{12} \exp(-br_{12})$$

WF (6) is one of the variants of Slater orbitals with correlation factors.

As shown in Ref.⁸, these function give the lowest energies compared to calculations performed by other authors.^{9,10}

We obtained the lowest values of the singlet state energy using Gaussian orbitals in comparison with the authors of Ref.⁸⁻¹⁰ Energy values of triplet terms are not given in Ref.^{8,10} Therefore, the Table shows only the values of the triplet states energy obtained in this research and in Ref.⁹ The advantage of Gaussian functions is related to the ability to reduce the finding of the energy functional minimum to the variation of analytic functions with many variables. A large number of variational parameters in a Gaussian system are not an obstacle for accurate results with using modern computers. Due to the existence of analogues of atomic systems with two electrons in condensed matter: two-electron centers of large radius in two-dimensional crystals ((bi) excitons, D⁻ centers), the computation methods described in this article can be used to calculate the energy spectrum of such systems. Gaussian functions with correlation factors have been successfully

used to calculate both singlet and triplet terms of two-electron atoms with an arbitrary nuclear charge Z. The information about the spin state of the system is detected by automatically symmetrized WF (5). Singh⁸ proposed WFs that take into account the cusp conditions arising due to the Coulombic nature of external potential and electron–electron interaction, and the screening effects:

used for calculations the energies of atomic and molecular systems interacting with phonons in three-dimensional crystals.^{13,14}

Conclusion

The variational method based on Gaussian functions was used to calculate the energies of singlet and triplet states of two-dimensional H⁻ and He atoms. The received energies are the lowest in comparison with the ones obtained by other authors. The used method can be applied to calculate the energy of singlet and triplet states of the two-dimensional atoms in a magnetic field. In this case, the triplet state of H⁻ becomes stable. In magnetic fields, 2D atoms become anisotropic. This circumstance can easily be taken into account by the separation of components Gaussian WFs in the directions OX and OY. In this case, the anisotropy parameter should be introduced in the direction of the magnetic field in the 2D plane.

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Conflicts of interest

The author declares there is no conflict of interest.

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