Theoretical algorithm for fast calculation of interatomic bonds

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Interatomic bonds in solids are known to be the result of a balance of four interactions. This is a direct Coulomb interaction between nuclei (repulsion). And three quantum-averaged interactions: electrons with nuclei (attraction) and two interelectronic interactions - "direct" (repulsion) and "exchange" (attraction). The last two interactions make the main contribution to making of connected states, as the first two are practically compensated. The last two interactions will be considered below.

General formulation of the problem

In constructing the desired algorithm, the operator of the electronic subsystem of the monoatomic condensate of the crystalline type in the representation of the filling numbers [1, 2] was used (this representation is also known as the secondary quantization representation or as a field representation). Standard averaging on the vacuum state vector of the electronic subsystem was performed [3, 4, 5]. The result was the total energy of the interatomic interaction between a pair of atoms, one of which is in node $\mathbf{0}$ of the crystal lattice (at the origin), and the second - in its node $\mathbf{r}$:

$$W(\mathbf{r}) = \sum_{f \leq g} \left(Q_{fg}(\mathbf{r}) - R_{fg}(\mathbf{r}) \right). \qquad (1)$$

In this energy, the summation is performed for all quantum states f and g filled with electrons. But really only need to consider the terms that play a key role in making the connection. As a rule, this is the highest energy-filled electron state. Therefore, to analyze the possibility of formation bonds, energy (1) will be analyzed in a simpler form:

$$W_f(\mathbf{r}) = Q_f(\mathbf{r}) - R_f(\mathbf{r}), \qquad (2)$$

where f is the standard set of hydrogen quantum numbers: $f = \{n, l, m\}$ for the energy highest electron filled state (n – principal, l – orbital, m – azimuthal quantum numbers). The first term in (2) denotes the quantum-averaged Coulomb repulsion between electrons:

$$Q_f(\mathbf{r}) = \iiint_{\infty}^{\infty} |\varphi_f(\mathbf{r}_2)|^2 d^3 r_2 \iiint_{\infty}^{\infty} q(|\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{r}|)|\varphi_f(\mathbf{r}_1)|^2 d^3 r_1, \qquad (3)$$

and the second term (together with the sign) means a quantum-averaged exchange attraction between them:

$$R_f(\mathbf{r}) = \iiint_{-\infty}^{\infty} \varphi_f^*(\mathbf{r}_2)\varphi_f(\mathbf{r}_2 - \mathbf{r})d^3 r_2 \iiint_{-\infty}^{\infty} q(|\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{r}|)\varphi_f^*(\mathbf{r}_1)\varphi_f(\mathbf{r}_1 + \mathbf{r})d^3 r_1. \qquad (4)$$

In the definitions (3), (4) the notation is used: $q(|\mathbf{p}|) \equiv q(p) = 2R_y/p$. Coulomb factor. R_y denotes the Rydberg energy: $R_y = e^2/(2a_B)$. Bohr radius is denoted by a_B. All quantities in (3), (4) are formulated in dimensionless representation. In particular, dimensionless spatial variables r_1, r_2, r are formulated in units of the Bohr radius and are related to the dimensional distances R_1, R_2, R by the obvious relations:

$$R_1 = r_1 a_B, \qquad R_2 = r_2 a_B, \qquad R = r a_B. \qquad (5)$$

The functions $\varphi_f(\mathbf{r}_i)$ are wave functions of a single-electron ion in the state f, which are centered by the lattice vector $\mathbf{0}$, and $\varphi_f(\mathbf{r}_i \pm \mathbf{r})$ are similar functions, but centered by the lattice vectors $\pm\mathbf{r}$. Abbreviated entry is used:

$$d^3 r_i = r_i^2 \sin\theta_i \, dr_i d\theta_i d\phi_i.$$

Next, energy (2) will be analyzed as a basis for constructing an algorithm for fast calculation of interatomic bonds.

Algorithm for fast calculation of interatomic bonds

The algorithm is based on approximate analytical calculations of integrals (3), (4). One of such approximations is the approximation of the far zone: $r_i \ll r$. Here such an approximation can be applied because the functions $\varphi_f(\mathbf{r}_i)$ decrease rapidly (exponentially) with increasing r_i already at distances of several Bohr radii. At the same time, the functions $\varphi_f(\mathbf{r}_i \pm \mathbf{r})$ and the Coulomb factor $q(|\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{r}|)$ almost unchanged at these distances and, if the condition $r_i \ll r$ is satisfied, they can be considered constants. According to this approximation, the integral (3), taking into account the fact that the functions $\varphi_f(\mathbf{r}_i)$ are normalized to unity, takes the form:

$$Q_f(\mathbf{r}) \equiv q(r) = 2R_y/r,$$

and the integral (4) is reduced to:

$$R_f(\mathbf{r}) = q(r)I_f(\mathbf{r})\varphi_f(\mathbf{r})\varphi_f(-\mathbf{r}),$$

where, taking into account only the linear contributions r_i/r under the sign of the square root in the Coulomb factor $q(|\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{r}|) = 2R_y/|\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{r}|$, we have the following definition:

$$I_f(\mathbf{r}) \equiv \iiint_{-\infty}^{\infty} \varphi_f^*(\mathbf{r}_2)d^3 r_2 \iiint_{-\infty}^{\infty} \frac{\varphi_f^*(\mathbf{r}_1)}{\sqrt{1 + 2\frac{r_1}{r}\cos\beta_1 - 2\frac{r_2}{r}\cos\beta_2}} d^3 r_1. \qquad (6)$$

The angles β_i between the vectors $\mathbf{r}_i$ and $\mathbf{r}$ are determined by the relations:

$$\cos\beta_i = \cos\theta \cos\theta_i + \sin\theta \sin\theta_i \cos(\phi - \phi_i). \qquad (7)$$

Here θ and ϕ are the angles that determine the projections of the vector of the interatomic distance $\mathbf{r}$ on the axis of the selected coordinate system, and θ_i and ϕ_i are similar angles for the vectors $\mathbf{r}_i$.

Despite the small value of terms $2(r_i/r)\cos\beta_i$ they cannot be neglected under the sign of the root in (6), because they depend on the angles θ_i and ϕ_i, which provides the correct finding of the factors $I_f(\mathbf{r})$.

Now definition (2) takes a more concrete form:

$$W_f(\mathbf{r}) = \frac{2R_y}{r}\left(1 - I_f(\mathbf{r})\varphi_f(\mathbf{r})\varphi_f(-\mathbf{r})\right). \qquad (8)$$

To further, it is necessary to indicate the explicit form of wave functions $\varphi_f(...)$. Considering that:

$$\varphi_f(\mathbf{r}) \equiv \varphi_{n,l,|m|}(\boldsymbol{\rho}) = a_{n,l,|m|}R_{n,l}(\rho)Y_{l,|m|}(\theta,\phi);$$

where

$$\rho = \frac{2z}{n}r; \qquad a_{n,l,|m|}^2 = \frac{2l + 1 (l - |m|)! (n - l - 1)!}{8\pi n (l + |m|)! (n + l)!} \qquad (9)$$

and $R_{n,l}(\rho)$ and $Y_{l,|m|}(\theta,\phi)$ are standard radial and angular parts of the wave hydrogen function (for $Y_{l,|m|}(\theta,\phi)$ instead of the notation $\varphi_f(...)$ we will use. Therefore, we will use the notation $\varphi_f^*(...)$). In (9) z is the charge number of condensate atoms. Expression (8), after some transformations, can lead to a completely dimensionless form:

$$V_{n,l,|m|}(\rho) = \frac{1}{\rho}\left(1 - \Gamma_{n,l,|m|}\rho^6 R_{n,l}^2(\rho)\right). \qquad (10)$$

There

$$V_{n,l,|m|}(...) = \frac{W_f(...)}{4zR_y/n}; \qquad \Gamma_{n,l,|m|} = a_{n,l,|m|}^4 S_{n,l,|m|}(\theta_0,\phi_0)Y_{l,|m|}^2(\theta_0,\phi_0). \qquad (11)$$

The factor $S_{n,l,|m|}(\theta_0,\phi_0)$ is an integral averaged over the variable ρ:

$$\iiint_{-\infty}^{\infty} \varphi_{n,l,|m|}(\rho\boldsymbol{\eta}_2)d^3\eta_2 \iiint_{-\infty}^{\infty} \frac{\varphi_{n,l,|m|}(\rho\boldsymbol{\eta}_1)}{\sqrt{1 + 2\eta_1\cos\beta_1^{(0)} - 2\eta_2\cos\beta_2^{(0)}}} d^3\eta_1,$$

angles θ_0, ϕ_0 is the direction that provides the negativeness of the second term in (10), and the notation $\beta_i^{(0)}$ emphasizes the fact that the angles β_i, which are defined in (7), depend of the angles θ_0, ϕ_0. Note also that the new integration variables η_i have the definition: $\eta_i = \rho_i/\rho$, where the variables ρ_i are defined similarly to the variables ρ y (9): $\rho_i = 2zr_i/n$, and the vector record $\boldsymbol{\eta}_i$ means the vectorial equality: $\boldsymbol{\eta}_i = \{\eta_i, \theta_i, \phi_i\}$. The factor $S_{n,l,|m|}$ averaged over the variable ρ is not calculated in the algorithm for fast calculation of interatomic bonds. Therefore, the whole factor $\Gamma_{n,l,|m|}$ is considered in this algorithm as a phenomenological parameter and in each case is determined for physical reasons. Definition (10) is the basis for the algorithm for fast calculation of interatomic bonds in dimensionless form.

Some examples

Next, we consider examples of the use of dimensionless energy (10) for the analysis of interatomic bonds in the cases: $f = \{1,0,0\} \equiv 1S$, $f = \{2,0,0\} \equiv 2S$ and $f = \{2,1,m\} \equiv 2P$. The energies (10) for these three cases have the form:

$$V_{1S}(\rho) = \frac{1}{\rho}\left(1 - \Gamma_{1S}\,\rho^6\exp(-2\rho)\right); \quad V_{2S}(\rho) = \frac{1}{\rho}\left(1 - \Gamma_{2S}\,(2 - \rho)^2\rho^6\exp(-\rho)\right);$$

$$V_{2P}(\rho) = \frac{1}{\rho}\left(1 - \Gamma_{2P}\,\rho^8\exp(-\rho)\right)$$

These dependencies are shown in Figure 1 for the following values of phenomenological parameters $\Gamma_{\bullet\bullet}$:

$$\Gamma_{1S} = 0.693940255; \qquad \Gamma_{2S} = 0.000532; \qquad \Gamma_{2P} = 0.000297.$$

This choice of parameters provides the same depth of dimensionless potential energies of the interatomic interaction $V_{\bullet\bullet}(\rho)$ based on the supposition that they can be the same for any situation. In this case, the value $V_{\bullet\bullet}(\rho) = -0.0861$ was determined using (11) of the known for carbon condensate ($z = 6$ and $n = 2$) the value of the dimensional energies $W_f(\min) \cong -14$ eV (states $f = \{2S, 2P\}$). For hydrogen condensate, according to (11), the dimensionless value of energy -0.0861 corresponds to the energy -4.66662 eV. This energy is close enough to the binding energy in the hydrogen molecule (-4.477 eV).

Consider the energy $V_{1S}(\rho)$ for hydrogen condensate. Studies of the possibility of the existence of metallic hydrogen have been conducted since the 1970s. During this period, it was found that it can be formed at pressures of several million atmospheres (from 1 to ~ 4 at a typical value of ~ 3 million atmospheres). The figure shows (curve 1S) that for the formation of condensate by hydrogen atoms, they must overcome the potential barrier with height $V_{1S}(\max) = 0.13569$. According to definition (11), for $z = 1$ and $n = 1$ this corresponds to the dimensional energy $W_f(\max) \cong 7.345$ eV.

On the other side, they should approach the distance $\rho_{\max} = 6.45$, which, according to the definitions (9) and (5), for hydrogen corresponds to the distance $R_{\max} = 1.613$ Å. Knowing these values, it is possible estimate the pressure required to overcome the potential barrier by the formula: $P > W_f(\max)/R_{\max}^3$. This estimate gives a value of $P > 2.8$ million atm. This fits into the experimental range and is a value rather close to the typical value (~ 3 million atmospheres).

Now consider the energies $V_{2S}(\rho)$, $V_{2P}(\rho)$ for carbon condensates. First of all, it is noteworthy that both dependences are quite close, which is physically correct for the carbon condensates with different hybridizations of 2S and 2P states. As can be seen from the figure, there are also potential barriers in both dependences, the average dimensionless height of which is $V_{2S,2P}(\max) = 0.053$, This, according to (11), for carbon corresponds to the dimensional value $W_f(\max) = 8.618$ eV. For create to the carbon condensates is used to the sputtering method.
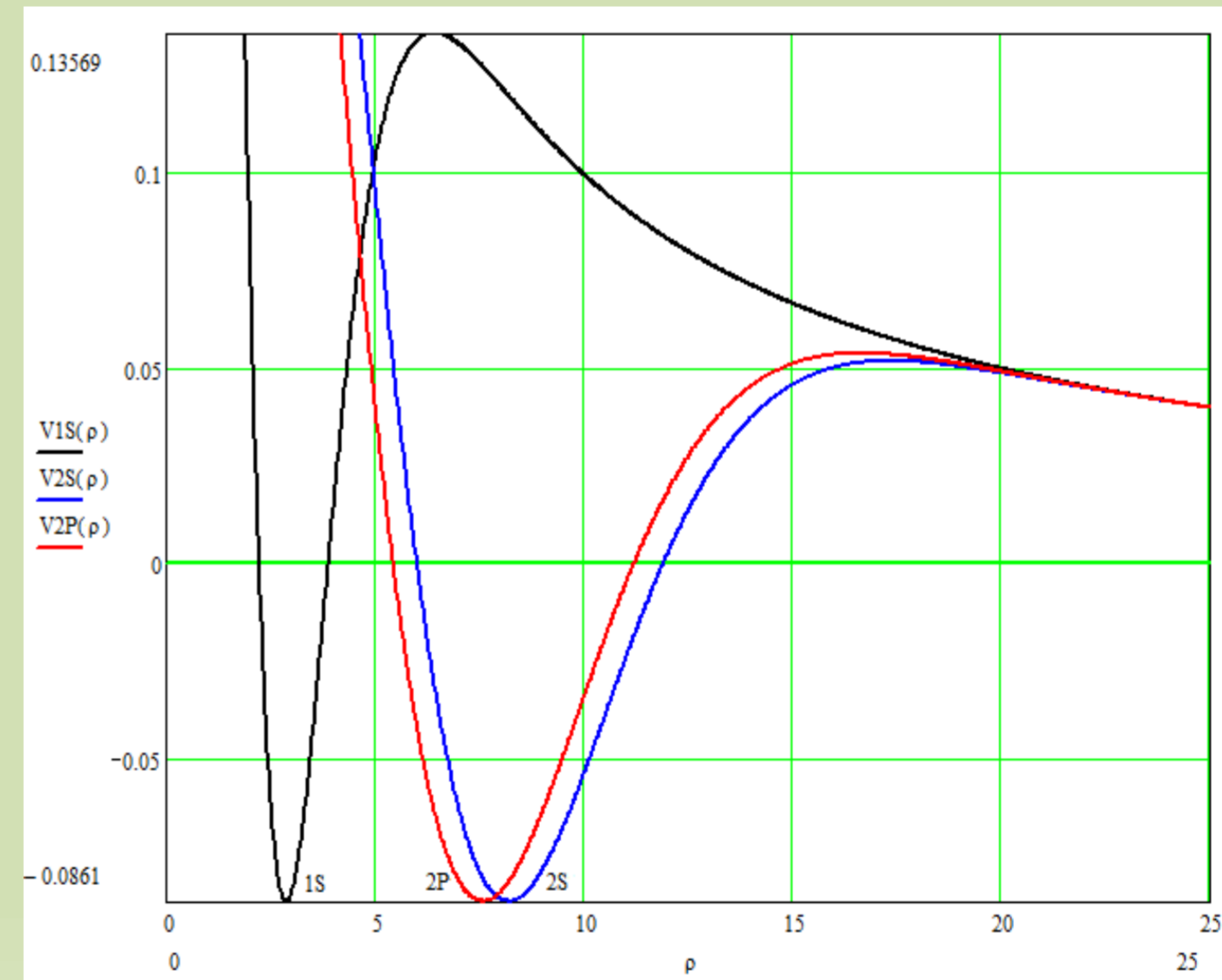

Fig. 1. Potential energies of interatomic interaction for formation of 1S – 1S, 2S – 2S and 2P – 2P bonds.

Obviously, the potential barrier of 8.618 eV needs to be get over to generate condensate by sputtering. Researches show that, really, at energies of irradiating carbon ions ~ 10 eV [6], condensates are formed, which, however, have a large proportion of polymer-like phase. But when the energy of carbon ions increases to ~ 50 eV [7], a diamond-like substance is formed.

Conclusions

The paper proposes a method for calculating the potential energy of interatomic interaction, an alternative to the use of significant computer resources. The algorithm was tested on the example of 1S – 1S, 2S – 2S and 2P – 2P bonds, what characteristic, in particular hydrogen (1S) and carbon (2S, 2P).

The developed algorithm also confirms the presence of potential barriers to the formation of interatomic bonds. Their presence explains some known facts. In particular, the estimates made on the basis of the algorithm confirm the conditions for the formation of metallic hydrogen and carbon condensates by ion sputtering.

References

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