On the origin of bonding in metals: sodium and chromium as case studies

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Abstract

The bonding in metals is analysed within the framework of the PATMOS (Perturbed AToms in MOlecules and Solids) model. The binding energy per atom is written as a sum of a distortion energy of the atom and the partitioned interaction energy comprising Coulombic, exchange and correlation terms. On the basis of calculations on one-dimensional arrays of sodium and chromium atoms, the following conjecture is suggested. Metals are made of weakly interacting atoms, i.e. perturbed atoms. A proper description of bonding requires an unrestricted Hartree-Fock wave function as the basic approximation. Metals and molecules have in common the predominance of the Coulombic interatomic interaction energy. Electron correlation is of paramount importance.

KEYWORDS
PATMOS model, energy partitioning, electron correlation, metals, bonding

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INTRODUCTION

Metallic bonding is apparently very different from bonding in polyatomic molecules. The latter is localized and directional. For a huge class of molecules, it can be described by localized electron-pair bonds. This picture of bonding is not easily transferred to a metal. For an alkali metal with a bcc-structure, there are eight nearest-neighbour atoms for a particular atom, but only one valence electron for each atom. Hence, a system of electron-pair bonds for the metal is indeed difficult to imagine. To cope with this enigma it is customary to suppose that a metal is characterized by a delocalized "sea" of electrons and that this "sea" of negative charge holds the atoms together. The corresponding mathematical model is Hartree-Fock theory with delocalized orbitals, i.e. canonical Hartree-Fock orbitals. However, within the one-determinant approximation, the wave function is invariant with respect to a unitary transformation of the orbitals. A delocalized picture can be transferred to a localized picture. Accordingly, the original problem of explaining bonding is as puzzling as before. The scientific community has then more or less disregarded this particular problem and instead focused on what can be obtained by molecular orbital theory with delocalized orbitals. An extensive body of scientific work demonstrates the success of this approach.

One of the difficulties of explaining bonding in metals can be traced back to a simplistic interpretation of the electron-pair bond concept. It is often interpreted as if electrons in complexes prefer to stick together in pairs. However, electrons repel each other, and left to themselves they separate. As for the ground state of a system, electrons try to come as close as possible to the nuclei in accordance with the Pauli exclusion principle. For localized orbitals we might interprete the Pauli principle as stating that two electrons with different spins can occupy the same part of the physical space. In order to obtain the lowest possible total energy for the system, the electrons arrange themselves in such a way that they are close to a nuclues or a pair of nuclei. In electron-pair bonds an electron of an atom is shifted towards the nucleus of a neighbouring atom, and vice versa. This particular feature of the electron-pair bonding is demonstrated in a work by Røeggen and Gao[1]. By moving away from the paring concept but keeping its physical content of the bonding, i.e. shifting of electrons in direction of neightboring atoms, bonding in metals might be more easily

understood.

Another key to understand bonding in metals is related to the electron density. The density in metals is not very different from the sum of the atomic densities of isolated atoms put in the positions of the nuclei of the metal. Hence, the atomic wave-functions are only modestly distorted in forming the metal. This fact has an important corollary. If one uses restricted Hartree-Fock in the study of metals, which implies doubly occupied orbitals, this feature of the metallic bond cannot be disclosed. Therefore, one should preferably use unrestricted Hartree-Fock as a basic approximation in describing metals since it is essential to have one spatial orbital for each valence electron.

In this work we shall adopt the PATMOS model[1,2] (Perturbed AToms in MOlecules and Solids) to analyse bonding in metals. The concept of perturbed atoms is ideally suited for such an analysis. The bonding energy per atom can be calculated in terms of distortion energies for the atoms involved and Coulomb, exchange and correlation energies between pair of atoms.

The structure of the article is as follows: The second section is devoted to a short description of the PATMOS model adapted to periodic systems. In the third section we present our studies on sodium and chromium.

THE PATMOS MODEL FOR PERIODIC SYSTEMS

The detailed description of the PATMOS model is given in our previous works[1,2]. Here we present what is of particular relevance for periodic systems: the energy partitioning, the modeling of an infinite structure by a finite set of unit cells, the use of a specific and local basis set for each atom and a localization procedure appropriate for periodic systems.

Energy partitioning

The PATMOS energy can be partitioned in the following way

$$E^{\text{PATMOS}} = \sum_{A=1}^{N_{\text{atoms}}} (E_A^{\text{UHF}} + E_A^{\text{corr}}) + \sum_{A<B}^{N_{\text{atoms}}} (E_{AB}^{\text{Coul}} + E_{AB}^{\text{exch}} + E_{AB}^{\text{corr}}) + \sum_{A<B<C}^{N_{\text{atoms}}} E_{ABC}^{\text{corr}} + \cdots . \quad (1)$$

In Eq. (1) N_{atoms} denotes the number of atoms in the physical model, E_A^{UHF} and E_A^{corr} are respectively the unrestricted Hartree-Fock (UHF) energy and the correlation energy for atom A, E_{AB}^{Coul} and E_{AB}^{exch} are respectively the Coulomb and exchange part of the interaction energy between the atoms A and B, and E_{AB}^{corr} is the correlation energy between the same atoms. Effective atomic energies can be introduced

$$E^{\text{PATMOS}} = \sum_{A=1}^{N_{\text{atoms}}} E_A^{\text{eff}}, \tag{2}$$

where

$$E_A^{\text{eff}} = E_A^{\text{UHF}} + E_A^{\text{corr}} + \frac{1}{2} \sum_{B \neq A}^{N_{\text{atoms}}} (E_{AB}^{\text{Coul}} + E_{AB}^{\text{exch}} + E_{AB}^{\text{corr}})$$

$$+ \frac{1}{3} \left\{ \sum_{\substack{B,C \\ A<B<C}}^{N_{\text{atoms}}} E_{ABC}^{\text{corr}} + \sum_{\substack{B,C \\ B<A<C}}^{N_{\text{atoms}}} E_{BAC}^{\text{corr}} + \sum_{\substack{B,C \\ B<C<A}}^{N_{\text{atoms}}} E_{BCA}^{\text{corr}} \right\} + \cdots . \tag{3}$$

An important term for a periodic system is the sum of effective atomic energies for the atoms in the reference cell:

$$E_{\text{uc}}^{\text{PATMOS}} = \sum_{A=1}^{N_{\text{atoms}}^{\text{uc}}} E_A^{\text{eff}}, \tag{4}$$

In Eq. (4) $N_{\text{atoms}}^{\text{uc}}$ is the number of atoms in the unit cell. As we increase the number of unit cells in the physical model, $E_{\text{uc}}^{\text{PATMOS}}$ should converge to the corresponding value for the infinite system.

In this work we are interested in the binding energy per atom:

$$E_A^{\text{bind}} = E_A^{\text{eff}} - E_A^{\text{iso}}, \tag{5}$$

where E_A^{iso} is the energy of the isolated atom. Then it follows from Eq. (3)

$$E_A^{\text{bind}} = \Delta_A^{\text{dist}} + E_{A,\text{inter}}^{\text{Coul}} + E_{A,\text{inter}}^{\text{exch}} + E_{A,\text{inter}}^{\text{corr}} \tag{6}$$

where

$$\Delta_A^{\text{dist}} = E_A^{\text{UHF}} + E_A^{\text{corr}} - E_A^{\text{UHF,iso}} - E_A^{\text{corr,iso}}, \tag{7}$$

$$E_{A,\text{inter}}^{\text{Coul}} = \frac{1}{2} \sum_{B \neq A}^{N_{\text{atoms}}} E_{AB}^{\text{Coul}}, \tag{8}$$

$$E_{A,\text{inter}}^{\text{exch}} = \frac{1}{2} \sum_{B \neq A}^{N_{\text{atoms}}} E_{AB}^{\text{exch}}, \tag{9}$$

$$E_{A,\text{inter}}^{\text{corr}} = \frac{1}{2} \sum_{B \neq A}^{N_{\text{atoms}}} E_{AB}^{\text{corr}} + \frac{1}{3} \left\{ \sum_{\substack{B,C \\ A<B<C}}^{N_{\text{atoms}}} E_{ABC}^{\text{corr}} + \sum_{\substack{B,C \\ B<A<C}}^{N_{\text{atoms}}} E_{BAC}^{\text{corr}} + \sum_{\substack{B,C \\ B<C<A}}^{N_{\text{atoms}}} E_{BCA}^{\text{corr}} \right\} + \cdots. \tag{10}$$

The term Δ_A^{dist}, the distortion energy, represents the change in the energy of atom A in the complex due to the presence of the surrounding atoms. The interpretation of the terms in Eqs. (8–10) should be evident.

In this work we adopt the orbital energy incremental scheme, introduced by Nesbet[3], for calculating the correlation energy. Nesbet's original work has been refined by Stoll and coworkers[4–6], by Røeggen[7,8], and more recently by Bytautas and Ruedenberg[9]. A multireference incremental scheme has been introduced by Voloshina and Paulus[10] in a correlation treatment of bulk metals. As suggested by Røeggen and Gao[2], the correlation energy in the PATMOS model can be calculated by any size extensive correlation model. Work is under way to include a coupled-cluster model in our computer code.

The physical model

In calculations on periodic systems one has to replace the infinite system by a model comprising a finite number of unit cells: a reference cell and a certain number of nearest neighbour cells. On this finite set of unit cells we impose translation symmetry. We shall have exactly the same localized wave functions in the neighbour cells as in the reference cell. Hence, there is no "surface" effect in our physical model. In the optimization of the UHF wave function for the atoms in the reference cell, we modify the orbitals such that we have translation symmetry at each step of the iterative cycle. We denote the number of unit celss in the model as $N_{\text{model}}^{\text{uc}}$.

The PATMOS basis set procedure

In the recent work by Røeggen and Gao[2] a basis function (BF) region is defined as a unit cell and a certain number of nearest neighbour unit cells. The number of unit cells of the BF-region is denoted $N_{\text{bf}}^{\text{uc}}$. See illustration in Fig. 1. Two different atom-centered basis sets are associated with each nucleus, a large one, $\{\chi_\mu^{A,\text{lb}}; \mu = 1, \cdots, m_A^{\text{lb}}\}$, and a small one, $\{\chi_\mu^{A,\text{sb}}; \mu = 1, \cdots, m_A^{\text{sb}}\}$. The basis set for an atom in the reference cell is then

$$\begin{aligned}
\Omega_{\text{dual}}^A &= \{\chi_\mu^{A,\text{dual}}; \mu = 1, \cdots, m_A^{\text{dual}}\} \\
&= \{\chi_\mu^{A,\text{lb}}; \mu = 1, \cdots, m_A^{\text{lb}}\} \overset{\text{BF-region}}{\underset{B \neq A}{\bigcup}} \{\chi_\mu^{B,\text{sb}}; \mu = 1, \cdots, m_B^{\text{sb}}\}.
\end{aligned} \tag{11}$$

The spatial part of a spin orbital (α- or β-type):

$$\psi_i^A = \sum_{\mu=1}^{m_A^{\text{dual}}} U_{\mu,i}^{\text{dual}} \chi_\mu^{A,\text{dual}}. \tag{12}$$

The orbitals of the UHF wave functions are subjected to orthogonality constraints:

$$\langle \psi_i^{A,\alpha} | \psi_j^{B,\alpha} \rangle = \delta_{ij} \delta_{AB}, \tag{13}$$

$$\langle \psi_i^{A,\beta} | \psi_j^{B,\beta} \rangle = \delta_{ij} \delta_{AB}. \tag{14}$$

The constraints, Eqs. (13, 14), require special attention in optimization procedure since the orbitals of different atoms are expressed in different basis sets.

Localization of orbitals

Localization of orbitals associated with different atoms is a non-trivial problem. Standard localization procedure cannot be used since we have different basis sets for different atoms. Our approach is the following:

Let $P^{A,\text{dual}}$ denote the projection operator associated with the basis set Ω_{dual}^A, Eq. (11). The spatial part of an α-type orbital of an atom B in the BF-region of atom A

$$\psi_j^B = \sum_{\mu=1}^{m_B^{\text{dual}}} U_{\mu,j}^{B,\text{dual}} \chi_\mu^{B,\text{dual}}, j = 1, \cdots, N_B^\alpha. \tag{15}$$

Projection onto the basis set associated with atom A

$$\hat{\psi}_j^B = P^{A,\text{dual}}\psi_j^B, j = 1, \cdots, N_B^\alpha. \tag{16}$$

The set $\bigcup_{B \neq A}^{\text{BF-region}} \left\{ \hat{\psi}_j^B; j = 1, \cdots, N_B^\alpha \right\}$ is not necessarily orthogonal to the α-type orbitals of atom A. The set $\left\{ \hat{\psi}_j^B \right\}$ is therefore first made orthogonal to the α-type orbitals of atom A, followed by a symmetric orthonormalization yielding $\bigcup_{B \neq A}^{\text{BF-region}} \left\{ \tilde{\psi}_j^B; j = 1, \cdots, N_B^\alpha \right\}$.

The next step is symmetric localization of the set $\left\{ \psi_i^A; i = 1, \cdots, N_A^\alpha \right\} \bigcup_{B \neq A}^{\text{BF-region}} \left\{ \tilde{\psi}_j^B; j = 1, \cdots, N_B^\alpha \right\}$. The resulting orbitals for atom A are then the proper localized orbitals.

CASE STUDIES

In this preliminary study of bonding and localization we restrict our attention to one-dimensional periodic systems. Two- and three-dimensional systems require further approximations in order to be computational feasible. We have chosen sodium and chromium as two different types of metals to be considered.

Our code requires family-type basis sets. Further, the exponents are all drawn from the same set of universal type exponents, i.e. $\left\{ \eta_k = \alpha\beta^{k-1}, k = 1, \cdots, k_{\max} \right\}$. The parameters defining the basis sets are given in Table 1. The correlation energy is calculated according to the Nesbet scheme truncated at the 2-electron FCI (full configuration interaction) level. We use an integral threshold of 10^{-7} E_h for the Cholesky decomposition of the two-electron integral matrix[11]. For the determination of the UHF wave function we have always $N_{\text{model}}^{\text{uc}} = N_{\text{bf}}^{\text{uc}}$.

Na atoms

The one-dimensional array of Na atoms has an equal nearest neighbour distance of $r_{\text{Na1,Na2}} = 7.021922$ bohr, the experimental equilibrium distance of nearest neighbour atoms in bcc solid sodium[12]. The basis sets adopted are uncontracted GTF (Gaussian type functions), a $(18s12p)$ for the small basis and $(18s12p4s3f1g)$ for the large basis. The s- and p-type functions are identical for the two basis sets. The parameters defining the basis sets are given in Table 1.

The bonding picture is described by charge centroids and charge ellipsoids[1,13]. The core orbitals, i.e. $1s$, $2s$ and $2p$ orbitals, are practically unchanged compared to the corresponding orbitals of the isolated atom. The $3s$ valence orbital on each atom is elongated along the "bond" axis (x-axis) and contracted along the y- and z-axis. See Fig. 2. The longest and shortest half axes are respectively 2.9992 bohr and 2.5501 bohr. This should be compared with 2.5846 bohr for the half axes of the spherical symmetric $3s$ orbital of the isolated atom. There is a small shift of the $3s$ orbital towards the second nucleus in the reference cell. The $3s$ α-type orbital has the following charge centroid: $(0.0016, 0.0000, 0.0000)$ bohr. This shift is due to the finite number of unit cells of the physical model. As is evident from Fig. 2, atom 1 has one atom less on the left hand side than on the right hand side. However, the localized picture of the bonding is very clear. The electron density of an atom is shifted in the direction of the neighbouring atoms.

In Table 2 we consider the convergence property of the model with respect to the model parameters $N_{\mathrm{model}}^{\mathrm{uc}}$ and $N_{\mathrm{bf}}^{\mathrm{uc}}$. For a fixed value of $N_{\mathrm{bf}}^{\mathrm{uc}} = 3$, we notice that the UHF energy, i.e. $E_{\mathrm{uc}}^{\mathrm{UHF,eff}}$, is converged when we include the first and second nearest neighbour (NN) unit cells in the model. The PATMOS energy, i.e. $E_{\mathrm{uc}}^{\mathrm{PATMOS,eff}}$, is also close to convergence. The difference in energy when we use the two different parameter sets ($N_{\mathrm{model}}^{\mathrm{uc}} = 7$, $N_{\mathrm{bf}}^{\mathrm{uc}} = 3$) and ($N_{\mathrm{model}}^{\mathrm{uc}} = 5$, $N_{\mathrm{bf}}^{\mathrm{uc}} = 3$) is only -0.000006 E_h. On the other hand, we have a slight larger deviation when we increase the basis set region. The difference in energy related to the two parameter sets ($N_{\mathrm{model}}^{\mathrm{uc}} = 5$, $N_{\mathrm{bf}}^{\mathrm{uc}} = 5$) and ($N_{\mathrm{model}}^{\mathrm{uc}} = 5$, $N_{\mathrm{bf}}^{\mathrm{uc}} = 3$): 0.000018 E_h and 0.000020 E_h for $E_{\mathrm{uc}}^{\mathrm{UHF,eff}}$ and $E_{\mathrm{uc}}^{\mathrm{PATMOS,eff}}$, respectively.

In Table 3 we look at the different contributions to the binding energy per atom from different neighbouring unit cells. We notice the rapid convergence with respect to the distance from the reference cell. By using the magnitude of the Coulombic contribution as the energy unit, the last line of Table 3 gives an instructive picture of the binding in a one-dimensional array of Na atoms. The dominant attractive contribution is the Coulombic term. But this negative term is cancelled by the positive distortion energy. The exchange term yields a small attractive term such that the system is bounded at the UHF level. The correlation energy is of paramount importane in order to obtain a reliable binding energy. Its relative value is -0.81 compared with the binding energy per atom of -0.92. However, it should

be kept in mind that the Nesbet hierarchy truncated at the 2-electron FCI level, typically overestimated the correlation energy with 10–15%. But for this particular system, based on FCI calculated on Li clusters[1], we believe that the error due to the disregard of 3-electron and higher order FCI terms in the Nesbet hierarchy, can be safely neglected for this system.

In this work we present mainly results for one-dimensional periodic systems. However, we have one preliminary UHF result on a two-dimensional lattice of Na atoms. We have included in the physical model 1 NN and 2 NN unit cells, i.e. $N_{\text{model}}^{\text{uc}} = 9$. For the basis function region we have the same number of unit cells, i.e. $N_{\text{bf}}^{\text{uc}} = 9$. The distance between the nearest neighbour atoms was intended to be the same as in the one-dimensional case. The charge centroids for the $3s$ orbitals: $(0.10, 0.11, 0.00)$ bohr and $(4.86, 4.83, 0.00)$ bohr. The half axes of the $3s$-ellipsoids: $\Delta l_x = \Delta l_y = 3.04$ bohr and $\Delta l_z = 2.43$ bohr. The half axes for the $3s$-ellipsoid for the isolated atom is 2.5846 bohr. See Fig. 3 for a pictorial representation. We notice the expansion of the $3s$ orbital in the direction of the neighbouring atoms. Unfortunately, it has not been feasible for us to calculate the correlation energy. But we have the binding energy per atom at UHF level: 0.002260 E_h. This value can be compared with the corresponding quantity for the one-dimensional case: 0.001958 E_h. Hence, increased binding as we move from a one-dimensional lattice to a two-dimensional lattice.

One-dimensional array Cr atoms

Among the transition metals chromium is a great challenge from a theoretical point of view. To obtain accurate values for the spectroscopic constants of the Cr_2 molecule is a formidable computational task. An extensive discussion on this problem is given in the recent work by Vancoillie et al.[14]. The core of the problem is the non-bonding of the molecule at the Hartree-Fock level. This implies that the correlation energy must be calculated very accurately. For a one-dimensional array of Cr atoms, it turns out that in the PATMOS model the system is only weakly non-bonded at the UHF level. The correlation energy is still very important, but not in the same critical way as in the diatomic molecule.

The one-dimensional array of Cr atoms has an equal nearest neighbour distance of $r_{\text{Cr1,Cr2}} = 4.72089$ bohr, the experimental equilibrium distance of nearest neighbour atoms in bcc solid chromium[12]. The basis sets adopted are uncontracted GTF, a $(15s9p6d)$ for

the small basis and $(15s9p6d4f2g)$ for the large one. The s-, p- and d-type functions are identical for the two basis sets. Paramters defining the basis setws are given in Table 1. The electron configuration for the atoms: $(1s^22s^22p^63s^23p^64s^13d^5)$. In the reference cell all valence orbitals of atom 1 are α-type orbitals, and all valence orbitals of atom 2 are β-type orbitals.

The bonding picture is described by charge centroids and charge ellipsoids. The core orbitals, i.e. $\{1s^22s^22p^63s^23p^6\}$, are practically unchanged compared with the orbitals of the isolated atom. In Table 4 we give half axes and volumes of the ellipsoids, and kinetic energy for the valence orbitals. For the isolated atom we have the following volumes for the d orbitals: $\{2.4588, 2.4588, 2.4588, 2.4839, 2.5917\}$ bohr. The volume of the $4s$ ellipsoid is 52.3027 bohr^3. The kinetic energy for the $3d$ and $4s$ orbitals are respectively 4.97444 E_h and 0.61949 E_h. We notice that for the complex three $3d$ orbitals expand. They are bonding orbitals. Two $3d$ orbitals contract slightly. They are weakly antibonding orbitals. The $4s$ orbital contract and hence is antibonding. In Fig. 4 we have depicted the $4s$ ellipsoid and the ellipsoid of the $3d$ orbital which is mostly affected by the bonding. The charge centroids for respectively the d_1 ellipsoid and $4s$ ellipsoid are $(-0.0007, 0.0000, 0.0000)$ bohr and $(0.0035, 0.0000, 0.0000)$ bohr. As for the other d orbitals, the charge centroids have distances from the "mother" nucleus less than 0.00001 bohr.

In Table 5 we look at the convergence property of the model with respect to the model parameters, $N_{\text{model}}^{\text{uc}}$ and $N_{\text{bf}}^{\text{uc}}$. The difference in the effective PATMOS energy for the unit cell atoms is only -0.000006 E_h when we move from $(N_{\text{model}}^{\text{uc}} = 5, N_{\text{bf}}^{\text{uc}} = 3)$ to $(N_{\text{model}}^{\text{uc}} = 7, N_{\text{bf}}^{\text{uc}} = 3)$. On the other hand we have a largeer deviation when we change the basis function region. The difference in PATMOS energy is 0.000793 E_h when we move from $(N_{\text{model}}^{\text{uc}} = 5, N_{\text{bf}}^{\text{uc}} = 3)$ to $(N_{\text{model}}^{\text{uc}} = 5, N_{\text{bf}}^{\text{uc}} = 5)$. Hence, for this system high accuracy requires that both the first and the second nearest neighbour unit cells are included in the basis function region.

In Tables 6 and 7 we look at different contributions to the binding energy per atom from different neighbouring unit cells. We notice the rapid convergence with respect to the increasing number of unit cells included in the model. The "driving force" of the binding is the Coulombic interaction term. But electron correlation is important. The binding energy per atom and the interaction correlation term are of the same magnitude. The binding

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energy obtained by using ($N_{\text{model}}^{\text{uc}} = 7$, $N_{\text{bf}}^{\text{uc}} = 3$) and ($N_{\text{model}}^{\text{uc}} = 5$, $N_{\text{bf}}^{\text{uc}} = 5$) are very close, i.e. -0.030769 E_h and -0.030322 E_h, respectively. The orbitals included in the correlation calculation are $\{3s^2 3p^6 4s^1 3d^5\}$. As stated, the correlation energy is calculated according to the Nesbet scheme truncated at the 2-electron FCI level. If we suppose that the error in the calculated correlation energy due to neglected terms in the Nesbet hierarchy, is of the order 10%, we will have an error in the calculated binding energy of the same order.

CONCLUDING REMARKS

In this work we have focused on one-dimensional structures of sodium and chromium atoms. However, we have also some preliminary calculations on potassium and vanadium. The localization of the valence orbitals for these atoms are similar to what has been presented for sodium and chromium. Hence, supporting our conjecture about the bonding in metals. On the other hand, we have a large number of calculations on lithium, both one-, two- and three-dimensional periodic structures. Lithium has in fact been our selected element for testing our ideas about metallic bonding. These calculations contradicted our picture of metallic bonding as advocated in this work. For the lithium systems the bonding seemed to be of the diatomic type, i.e. a shift of the $2s$ valence orbital towards one of the nearest neighbouring atoms. This lack of symmetry was very disturbing before we realised that lithium might in a sense be the odd metallic element. The extension of the core orbitals, measured by the charge ellipsoids, shows that the volume of the $1s$ ellipsoid for the Li atom is 0.2413 bohr^3 while the $2s$ ellipsoid for the Na atom has a volume of 0.5043 bohr^3. For this particular reason, and when we use a small number of unit cells in the physical model, the diatomic type of bonding might be more efficient than the metallic type of bonding, as demonstrated for sodium and chromium. The binding properties of lithium should therefore be discussed in a separate study.

   On the basis of this study we put forward the following conjecture about bonding in pure metals: First, metals comprise weakly interacting atoms. But since an atom is bonded to several neighbouring atoms, the binding energy can be large. Second, in order to have a proper description of the bonding, a UHF wave function is required as a root function

in a wave function model since the electron must be allowed to be close to their original nucleus, i.e. the nucleus of the isolated atom. Third, the mechnism of bonding in metals and molecules is similar with respect to the predominance of the interatomic Coulombic interaction. Fourth, electron correlation is of paramount importance for obtaining accurate binding energies.

In this work we have chosen the Nesbet hierarchy truncated at the 2-electron FCI level for calculating the correlation energy. The advantage of this approach is the possibility of using a large basis set. The disadvantage is the lack of coupling between the two-electron terms. The natural remedy is to include three- and four-electron FCI terms. But his last approach is quite cumbersome with an increasing number of electrons. The scheme which we shall include in our computer code is a combination of 2-electron FCI terms as in the Nesbet hierarch and a coupled cluster model. First, we calculate the 2-electron FCI terms for the system in question. Then we construct a set of natural orbitals (NOs) based on the 2-electron FCI terms. From this set we select the dominant NOs and use this set as basis functions in a coupled cluster calculation on the complex. This step is followed by a new calculation of the 2-electron FCI terms and with selected NOs as basis. The differene between the coupled cluster energy and the sum of the 2-electron FCI terms (based on NOs), is the proper coupling term. The sketch approach is very similar to the computational models Røeggen[8,15] used in the study of intermolecular interactions. We believe that the outlined procedure should be an accurate and reliable procedure for calculating the correlation energy for periodic systems.

FUNDING INFORMATION

RESEARCH RESOURCES

References

1. Røeggen, I., Gao, B., J. Chem. Phys., **2013**, 139, 094104.

2. Røeggen, I., Gao, B., J. Chem. Phys., **2018**, 148, 134118.

3. Nesbet, R. K., Adv. Chem. Phys., **1969**, 14, 1.

4. Stoll, H., Phys. Rev. B, **1992**, 46, 6700.

5. Stoll, H., J. Chem. Phys.,**1992**, 97, 8449.

6. Shukla, A., Dolg, M., Fulde, P., Stoll, H., Phys. Rev. B, **1998**, 57, 1471.

7. Røeggen, I., J. Chem. Phys., **1983**, 79, 5520.

8. Røeggen, I. In Correlation and Localization, Topics in Current Chemistry; Surján P. R., Eds.; Springer: Berlin, **1999**; Vol. 203, pp 89-103.

9. Bytautas, L., Ruedenberg, K., J. Phys. Chem. A, **2010**, 114, 8601.

10. Voloshina, E., Paulus, B., J. Chem. Theory Comput., **2014**, 10, 1698.

11. Røeggen, I., Johansen, T., J. Chem. Phys., **2008**, 128, 194107.

12. Emsley, J., The Elements; Oxford University Press: Oxford, **1994**.

13. Robb, M. A., Haines, W. J., Csizmadia, I. G., J. Am. Chem. Soc., **1973**, 95, 42.

14. Vancoillie, S., Malmqvist, P. Å., Veryazov, V., J. Chem. Theory Comput., **2016**, 12, 1647.

15. Røeggen, I., J. Chem. Phys., **2006**, 124, 184502.

Figure 1: Model of infinite, one-dimensional periodic system of unit cells. Reproduced from J. Chem. Phys. 148, 134118 (2018), with the permission of AIP Publishing.

Figure 2: Intersection between the xy-plane and the charge ellipsoids of the $3s$ α- and β-type orbitals of the atoms in the reference cell of a one-dimensional array of Na atoms. The number of unit cells in the model and the number of unit cells in the basis function region are, respectively, $N^{\mathrm{uc}}_{\mathrm{model}} = 5$ and $N^{\mathrm{uc}}_{\mathrm{bf}} = 5$. Half axes and distances in scale. Basis: $(sb/lb) = (18s12p/18s12p4d3f1g)$.

Figure 3: Intersection between the xy-plane and the charge ellipsoids of the $3s$ α- and β-type orbitals of the atoms in the reference cell of a two-dimensional lattice of Na atoms. The distance between the atoms in the reference cell is the experimental equilibrium distance of nearest neighbour atoms in bcc solid sodium[12]. The second atom is at the midpoint of the reference cell. The number of unit cells in the model and the number of unit cells in the basis function region are, respectively, $N^{\mathrm{uc}}_{\mathrm{model}} = 5$ and $N^{\mathrm{uc}}_{\mathrm{bf}} = 9$. Half axes and distances in scale. Basis: $(sb/lb) = (18s12p/18s12p4d3f1g)$. Dotted line for ellipsoid of $3s$ orbital for isolated atom.

Figure 4: Intersection between the xy-plane and the charge ellipsoids of the selected orbitals of the atoms of the reference cell of a one-dimensional array of Cr atoms. The selected $3d$-type orbital is the one mostly distorted. The number of unit cells in the model and the number of unit cells in the basis function region are, respectively, $N^{\mathrm{uc}}_{\mathrm{model}} = 5$ and $N^{\mathrm{uc}}_{\mathrm{bf}} = 5$. Half axes and distances in scale. Basis: $(sb/lb) = (15s9p6d/15s9p6d4f2g)$.
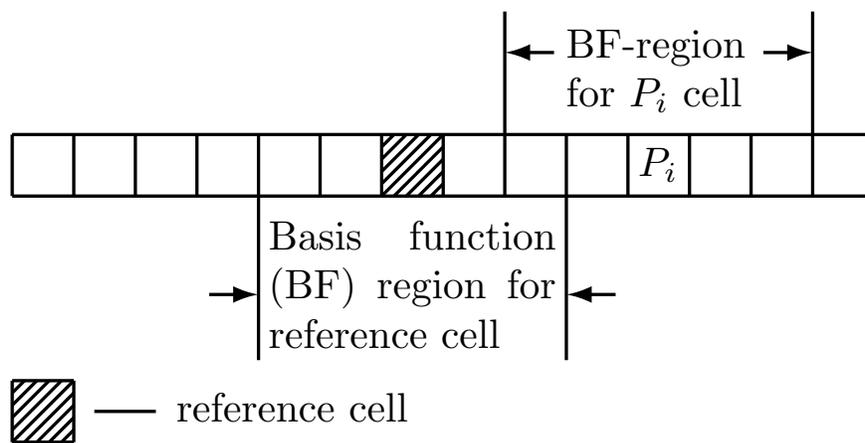
Figure 1
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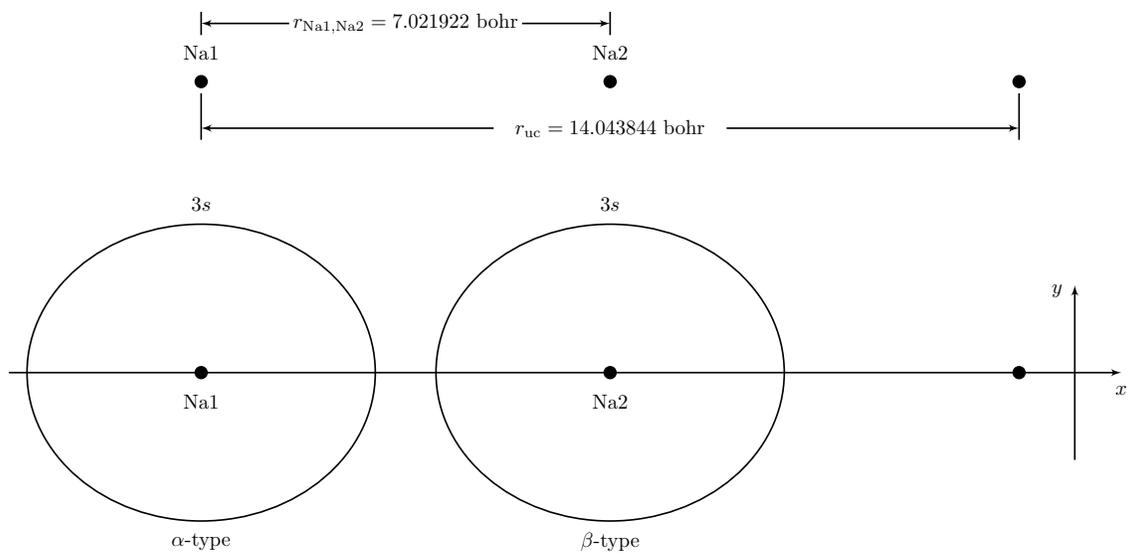
Figure 2
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α-type

β-type

Na1

Na2
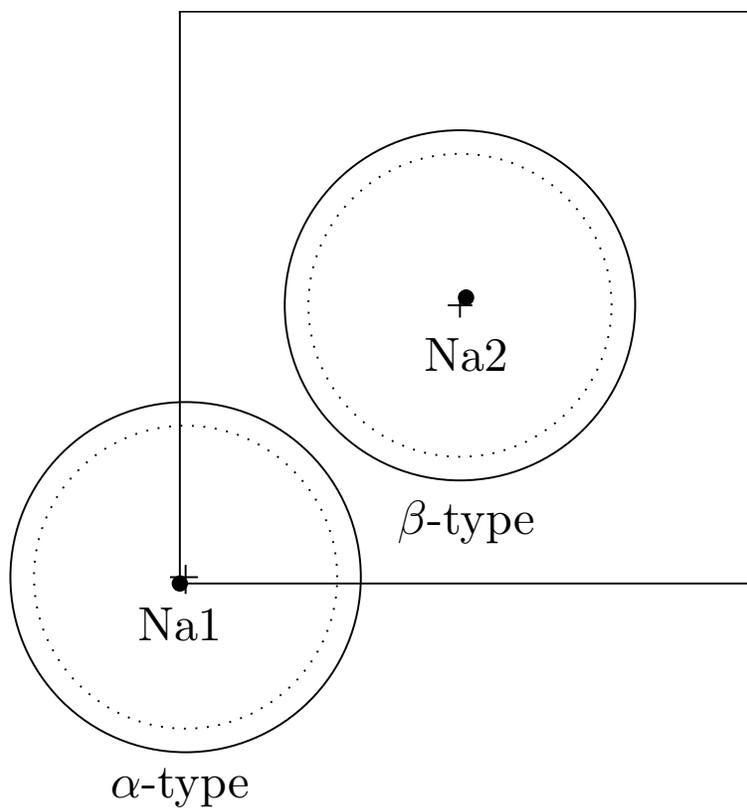
Figure 3
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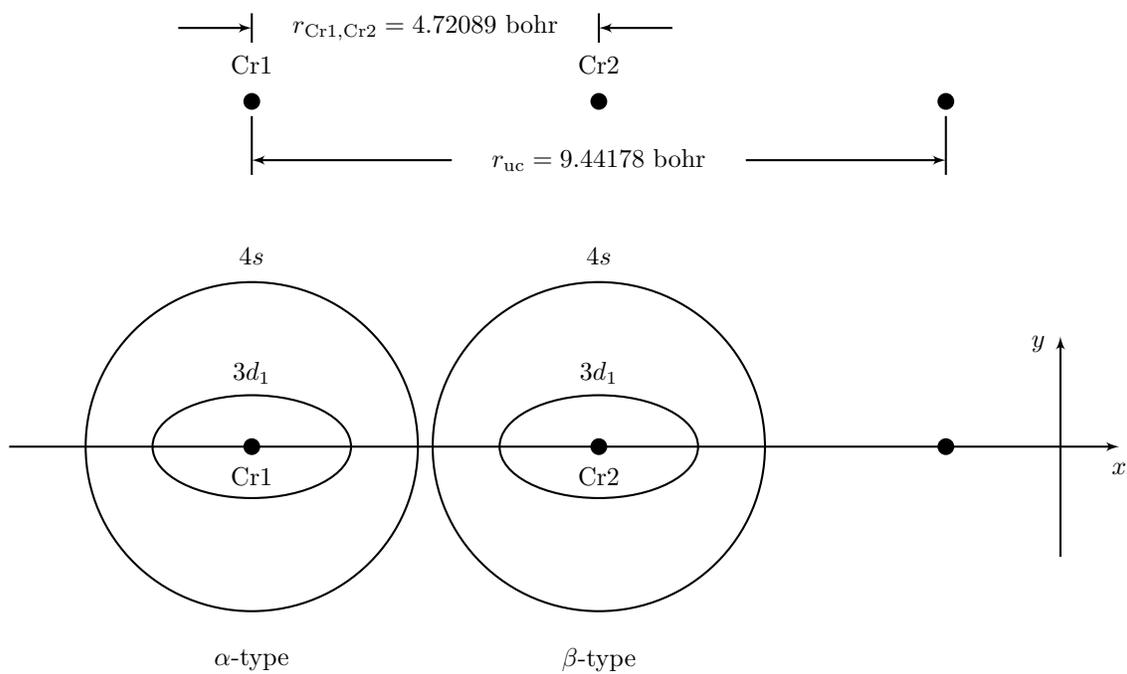
Figure 4
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Atoms/Basis	β	s	p	d	f	g
Cr $(15s9p5d4f2g)$	3.55	0.0153171	0.1930331	0.1930331	0.1930331	0.6852676
Na $(18s12p4d3f1g)$	2.32	0.0329964	0.0329964	0.0329964	0.0765517	0.177600

Table 1: Lowest exponents of the GTF-family basis sets used in this work ($\eta_k = \alpha\beta^{k-1}$).

$N_{\text{model}}^{\text{uc}}$	$N_{\text{bf}}^{\text{uc}}$	$E_{\text{uc}}^{\text{UHF,eff}}$ (sb/lb)	$E_{\text{uc}}^{\text{PATMOS,eff}}$ (sb/lb)
		(E_h)	(E_h)
3	3	-323.720858	-323.759758
5	3	-323.720858	-323.759890
7	3	-323.720858	-323.759893
5	5	-323.720832	-323.759870

Table 2: Effective unit cell energies as a function of model parameters for a one-dimensional array of Na atoms. Basis: $(sb/lb) = (18s12p/18s12p4d3f1g)$. Correlation model: Nesbet hierarchy including 2e-FCI. Electrons correlated: valence-core (intra), valence-valence, valence-core (inter). Nearest neighbour distance: 7.021922 bohr. Isolated atomic energy with basis $(18s12p4d3f1g)$: -161.864019 E_h.

Unit cells	$\Delta_{\text{Na1}}^{\text{dist}}$	$E_{\text{Na1,inter}}^{\text{Coul}}$	$E_{\text{Na1,inter}}^{\text{exch}}$	$E_{\text{Na1,inter}}^{\text{corr}}$	$E_{\text{Na1}}^{\text{bind}}$
	(E_h)	(E_h)	(E_h)	(E_h)	(E_h)
Ref. unit cell		-0.008342	-0.000887	-0.006704	
1-NN unit cells		-0.008770	-0.001260	-0.007205	
2-NN unit cells		-0.000016	-0.000005	-0.000045	
3-NN unit cells		-0.000001	-0.000000	-0.000001	
Total	0.017323	-0.017129	-0.002152	-0.013955	-0.015913
	(1.01)	(-1.00)	(-0.12)	(-0.81)	(-0.92)

Table 3: Contribution to the binding energy per atom from atoms in different unit celss for a one-dimensional array of Na atoms. Basis: $(sb/lb) = (18s12p/18s12p4d3f1g)$. $N_{\text{model}}^{\text{uc}} = 7$, $N_{\text{bf}}^{\text{uc}} = 3$.

Δl_x	Δl_y	Δl_z	V	$E_{\text{orb}}^{\text{kin}}$
(bohr)	(bohr)	(bohr)	(bohr^3)	(E_h)
1.3493	0.6987	0.6985	2.7589	4.79151
1.0643	0.5934	1.0278	2.7192	4.85968
1.0643	1.0279	0.5934	2.7196	4.85946
0.5860	1.0008	1.0008	2.4585	5.00330
0.5860	1.0007	1.0008	2.4585	5.00328
2.2584	2.2447	2.2447	47.6668	0.84384

Table 4: Half axes of charge ellipsoids, volume of charge ellipsoids and kinetic energy of the corresponding orbitals for the $3d$ and $4s$ orbitals of one of the atoms in the reference cell of a one-dimensional array of Cr atoms. Basis: $(sb/lb) = (15s9p6d/15s9p6d4f2g)$. The number of unit cell: $N_{\text{model}}^{\text{uc}} = N_{\text{bf}}^{\text{uc}} = 5$. Atoms along the x-axis.

$N_{\mathrm{model}}^{\mathrm{uc}}$	$N_{\mathrm{bf}}^{\mathrm{uc}}$	$E_{\mathrm{uc}}^{\mathrm{UHF,eff}}$ (sb/lb) (E_h)	$E_{\mathrm{uc}}^{\mathrm{PATMOS,eff}}$ (sb/lb) (E_h)
3	3	-2085.276065	-2086.499799
5	3	-2085.276065	-2086.500485
7	3	-2085.276065	-2086.500491
5	5	-2085.276354	-2086.499692

Table 5: Effective unit cell energies as a function of model parameter for a one-dimensional array of Cr atoms. Basis: $(sb/lb) = (15s9p6d/15s9p6d4f2g)$. Correlation model: Nesbet hierarchy including 2e-FCI. Electrons correlated: $(3s^2 3p^6 4s^1 3d^5)$. Nearest neighbour distance: 4.72089 bohr. Isolated atomic energy with basis $(15s9p6d4f2g)$: -1043.219862 E_h.

Unit cells	$\Delta^{\text{dist}}_{\text{Cr1}}$	$E^{\text{Coul}}_{\text{Cr1,inter}}$	$E^{\text{exch}}_{\text{Cr1,inter}}$	$E^{\text{corr}}_{\text{Cr1,inter}}$	$E^{\text{bind}}_{\text{Cr1}}$
	(E_h)	(E_h)	(E_h)	(E_h)	(E_h)
Ref. unit cell		-0.054251	-0.008833	-0.016607	
1-NN unit cells		-0.059394	-0.010677	-0.017238	
2-NN unit cells		-0.000492	-0.000081	-0.000113	
3-NN unit cells		-0.000004	-0.000001	-0.000000	
Total	0.136922	-0.114141	-0.019592	-0.033958	-0.030769
	(1.20)	(-1.0)	(-0.17)	(-0.30)	(-0.27)

Table 6: Contribution to the binding energy per atom from atoms in different unit cells for a one-dimensional array of Cr atoms. Basis: $(sb/lb) = (15s9p6d/15s9p6d4f2g)$. $N^{\text{uc}}_{\text{model}} = 7$, $N^{\text{uc}}_{\text{bf}} = 3$.

Unit cells	Δ_{Cr1}^{dist}	$E_{Cr1,inter}^{Coul}$	$E_{Cr1,inter}^{exch}$	$E_{Cr1,inter}^{corr}$	E_{Cr1}^{bind}
	(E_h)	(E_h)	(E_h)	(E_h)	(E_h)
Ref. unit cell		-0.054265	-0.008839	-0.016614	
1-NN unit cells		-0.059861	-0.010806	-0.017307	
2-NN unit cells		-0.000999	-0.000117	-0.000132	
Total	0.138618	-0.115125	-0.019762	-0.034053	-0.030322
	(1.20)	(-1.00)	(-0.17)	(-0.30)	(-0.27)

Table 7: Contribution to the binding energy per atom from atoms in different unit cells for a one-dimensional array of Cr atoms. Basis: $(sb/lb) = (15s9p6d/15s9p6d4f2g)$. $N_{model}^{uc} = N_{bf}^{uc} = 5$.