Electronic Structure of Crystalline Uranium Nitrides UN, U$_2$N$_3$ and UN$_2$: LCAO Calculations with the Basis Set Optimization

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Abstract. The results of LCAO DFT calculations of lattice parameters, cohesive energy and bulk modulus of the crystalline uranium nitrides UN, U$_2$N$_3$ and UN$_2$ are presented and discussed. The LCAO computer codes Gaussian03 and Crystal06 are applied. The calculations are made with the uranium atom relativistic effective small core potential by Stuttgart-Cologne group (60 electrons in the core). The calculations include the U atom basis set optimization. Powell, Hooke-Jeeves, conjugated gradient and Box methods are implemented in the author’s optimization package, being external to the codes for molecular and periodic calculations. The basis set optimization in LCAO calculations improves the agreement of the lattice parameter and bulk modulus of UN crystal with the experimental data, the change of the cohesive energy due to the optimization is small. The mixed metallic-covalent chemical bonding is found both in LCAO calculations of UN and U$_2$N$_3$ crystals; UN$_2$ crystal has the semiconducting nature.

1. Introduction

The crystalline uranium nitrides are intensively studied experimentally, as promising fuel materials for the Generation-IV fast reactors. The theoretical studies of these systems are difficult as they require to take into account the relativistic character of the U atom core electrons and strong electron-electron correlation. More, it is well known that the convergence of the self-consistent field procedure is difficult in the materials with closely-lying partially occupied metal f-orbitals [1].

The majority of non-empirical calculations are made on the actinide dioxides, both the perfect and defective, see [1-3] and references therein. Conversely, for nitrides, there are known to date mainly the calculations of UN made by the traditional for solid state theory methods: KKR [4], LMTO [5], Plane waves (PW) [6-8] and LAPW [9, 10]. Recent LCAO calculations [11, 12] allowed the more careful study of the mixed metallic-covalent chemical bonding in UN crystal.

The calculations on experimentally known relevant stoichiometric U$_2$N$_3$ and UN$_2$ crystalline compounds are made recently [7, 8] in PW basis. Recent LCAO UN$_2$ calculation [12] uses numerical atomic basis. To the best of our knowledge, no LCAO electronic structure calculations of crystalline U$_2$N$_3$ compounds have been performed so far.

In the three uranium nitrides mentioned the valence of U changes from 3 to 6. Comparative LCAO calculations of all the three crystals could allow the changes in chemical bonding with the U valence increase to be understood.

It is also important to answer on the following question – is it possible to use for U atom the free atom basis set (BS) corresponding to the pseudopotential chosen with removing the diffuse Gaussian type orbitals or it is necessary to optimize BS. Such an optimization requires a special optimization package. This package was generated by authors. It implements different algorithms of many variables function minimization and is external to the computer code for the crystal calculations.
In this paper we present and discuss the results of LCAO DFT calculations in the comparative study of UN, U$_2$N$_3$ and UN$_2$ crystals. The basis set optimization is made for UN crystal.

In Section 2 we consider the different methods which can be used for the BS optimization in solids.

In Section 3 we discuss the results of UN crystal calculations with the different choice of the uranium core effective potential and with use of the different Hamiltonians. Basing on the comparison of the results obtained for bulk properties of UN the relativistic small core effective potential of Stuttgart-Cologne group (SC60) is chosen.

In Section 4 the results of LCAO DFT (PW91) calculations of uranium nitrides UN, U$_2$N$_3$ and UN$_2$ are compared with those obtained in PW calculations. The comparison of the chemical bonding in three crystals is made. The influence of the U basis set optimization is studied for UN crystal.

2. Basis set choice and optimization

In the calculations of the heavy atom compounds, (such as uranium nitrides), the relativistic effective core potentials (RECP) are used to reduce the computational effort and take into account the relativistic effects for the core electrons. The different procedures of RECP construction for LCAO calculations have been suggested. We use here two small core RECP’s for U-atom: the energy-adjusted RECP by Stuttgart-Cologne (SC) group [13]. SC60 and the generalized shape-consistent RECP by Mosyagin-Titov (MT), MT60 [14]. 32 outermost uranium atom electrons are included in the valence shell (RECP for valence configuration $5s^25p^65d^106s^26p^66d^15f^{3}3j^2$). For comparison the large-core RECP MT78 was used ($5s, 5p$ and $5d$ electrons are included in the core).

**Table 1.** Diffuse primitive Gaussian exponents in basis set of uranium atom used with the Stuttgart-Cologne pseudopotential SC60 [13].

| GTF | $s$    | $p$    | $d$    | $f$    |
|-----|--------|--------|--------|--------|
| 1   | 0.071170 | 0.005000 | 0.073273 | 0.181420 |
| 2   | 0.030539 | 0.005000 | 0.005000 | 0.005000 |
| 3   | 0.005000 |

The corresponding to RECP basis sets are given in [13,14] as the linear combination of the Gaussian type functions (GTF), including both contracted and primitive GTF’s. In particular, the contracted part of U basis set (12s11p10d8f)/(8s7p6d4f) corresponding to RECP SC60 in the segmented contraction scheme, defines three $s$-type (5s, 6s, 7s), two $p$-type (5p, 6p), two $d$-type (5d, 6d) and one $f$-type (5f) orbitals, occupied by the valence electrons in the ground state of U atom. The rest (primitive) GTF’s are polarizing and diffuse orbitals (the exponents of diffuse Gaussians are given in Table 1). The diffuse orbitals are necessary to properly describe the tails of the free-atom wave functions. The basis sets $1s5p6d5f$ and $6s3p4d4f$ (not given here) correspond to the RECPs MT60 and MT78 and are also used in our calculations (see next section).

It is well known that for the crystal LCAO calculations the basis set of free atom has to be modified as the diffuse functions cause numerical problems because of the large overlap with the basis functions of the neighboring atoms in a dense-packed crystal [15-17]. In the calculations of crystals the diffuse exponents are simply removed or optimized to minimize the total energy per unit cell. For example, the detailed optimization of the basis set was made in the perovskites $\text{ATiO}_3$ ($A=$Sr, Ba, Pb) Hartree-Fock (HF) and DFT LCAO calculations [18] and allowed the available experimental data (the lattice parameters, the bulk modulus, the optical band gaps) to be well reproduced. BS optimization was made in [18] by the conjugated gradient method with a numerical computation of derivatives [19].

There exist different algorithms of many variables function minimization [19, 20]. The comparative study of their efficiency for the BS optimization in crystals is not made till now. The total electronic energy depends on chosen for optimization BS exponential parameters $\zeta=(\zeta_1, \zeta_2, \ldots, \zeta_n)$ via one- and two-electron integrals. It is not difficult to derive exact analytic expressions for energy derivatives with respect to the exponential parameters but the calculation of such derivatives requires evaluation of numerous integrals which otherwise would not arise in the course of electronic structure...
calculations. Use of analytic gradients presupposes serious modification of the integral part of available code for molecule or crystal calculations. In addition, calculations with analytic gradients can be very time-consuming. Therefore it seems reasonable to have external optimization package that calls the basic electronic structure calculation code only for energy evaluation when such an evaluation is required by the optimization routine. Such an approach seems to be quite general because any used in quantum chemistry LCAO code may be applied and its only drawback is numerical evaluation of energy derivatives if they are required.

When implementing optimization methods, it is necessary to choose between algorithms that need only evaluations of the energy and algorithms that also require evaluations of the energy derivatives.

One of the oldest and simplest methods of minimization without calculation of derivatives, which probably goes back to Gauss, is usually called the coordinate relaxation method. Unfortunately, the convergence of this method is usually very slow. Successful modification of this method was suggested by Hooke and Jeeves [20]. Their strategy includes local investigation of object function behavior in a neighborhood of a current point (exploring search) with subsequent selection of direction of descent with the aid of the information obtained on the stage of the exploring search (pattern search). This method was implemented in our BS optimization package and showed itself as a reliable and convenient optimization tool.

Much more sophisticated method of minimization without calculation of derivatives was developed by Powell [19] and is often called ‘the method of conjugate directions’. For convex quadratic function of $n$ variables

$$f(\zeta) = a + b^T \zeta + \frac{1}{2} \zeta^T H \zeta$$

(1)

two directions $\zeta_1$, $\zeta_2$ are called conjugate if they are orthogonal in the metric defined by positive definite symmetric matrix $H$, that is $\zeta_1^T H \zeta_2 = 0$. It is easy to see that if the minimization routine constructs at each step a direction conjugate to the preceding ones and along this direction exact 1-dimensional minimization is performed, then the minimum of the aforementioned quadratic function can be found in $n$ steps. In the case of arbitrary differentiable function the notion of conjugate directions is of a local character and has sense only in such a neighborhood of a current point where quadratic approximation of the function under consideration is valid.

Powell was the first who discovered a convenient strategy for generation of $n$ mutually conjugate directions without calculation of derivatives. Powell method is considered as one of the most efficient direct minimization methods but its convergence properties strongly depend on the precision of 1-dimensional minimization along the chosen direction. Note that Hooke-Jeeves method is less sensitive to the precision of line minimizations. Powell’s method accompanied by the line minimization routine due to Brent [19] is also included in our BS optimization package.

The simplest approach that uses the first derivatives of object function is certainly the steepest descent method in which the direction of descent coincides with the antigradient of the function to be minimized. Unfortunately, this method is famous by its slow convergence and is rarely used in concrete calculations. Methods combining conjugate and antigradient directions proved to be much more powerful. Such methods are called conjugate gradient methods and usually have good convergence characteristics. They require line minimization with the moderate precision but are rather sensitive to the precision of gradient evaluation. Following recommendations in [19], we included in our BS optimization package the Polak-Ribiere conjugate gradient routine with numerical evaluation of the first derivatives and Brent line minimization procedure. Evaluation of derivatives is performed iteratively until the prescribed precision is reached.

Till now it has been assumed that variables can take arbitrary real values. Sometimes, however, there are a priori limitations on the allowed values of independent variables. For example, electronic energy is not defined for negative values of BS exponential parameters and badly defined for their values less than 0.1. Optimization problem with limitations on the allowed values of independent variables is called the constrained optimization.

In our calculations we applied the program package which can be used for BS optimization with Gaussian03 and Crystal06 LCAO codes. Both codes allow the electronic structure of molecules and
crystals to be calculated. The minimization object function is the total energy (for a molecule) or the energy per unit cell (for a crystal). In the crystal calculations the constraint optimization was made – it was required that the BS exponential parameters are not less than 0.1. The optimization was performed only for primitive (uncontracted) GTFs. A posteriori the optimized primitive GTFs were used in the atomic basis, without any change of its contracted part.

As an example of the efficiency of BS optimization routines we performed the calculations of octahedral UF₆ neutral molecule and molecular ion UF₆⁺. For U atom RECP SC60 and the corresponding BS were applied, for F atom all electron BS 6-31+G* from [25] was used. The calculations were performed by Gaussian 03 code [21], the optimization was made for 14 of U-atom and 3 of F-atom uncontracted GTFs. The results of Powell and Hooke-Jeaves optimization methods are very close. As could be expected the former appeared to be more robust.

3. Computational details

Our LCAO calculations were made for the cubic uranium mononitride UN (rocksalt structure, two atoms per unit cell, space group Fm3m, Figure 1a), cubic uranium dinitride UN₂ (fluorite structure, three atoms per unit cell, space group Fm3m, Figure 1c), and more complicated U₂N₃ crystal (5 atoms per unit cell, hexagonal structure with the space group P3m1, Figure 1b: the three nitrogen atoms split into the symmetry-nonequivalent groups of one and two atoms).

![Figure 1. The structure of uranium nitrides: (a) UN, space group Fm3m; (b) U₂N₃, space group P3m1; (c) UN₂, space group Fm3m. U atoms – dark balls, N-atoms – light balls.](image)

We used two computer codes allowing the LCAO calculations of periodic systems: Gaussian03 [21] and Crystal06 [22]. The Monkhorst-Pack scheme [23] for 16×16×16 k-point mesh in the Brillouin zone (BZ) was applied. It was found that both codes give close results if the direct lattice summation is made up to 50 a.u. in Gaussian03 and the tolerances 8 8 8 16 are used in Crystal06 for the Coulomb and exchange integrals calculations.

As an example we compared the results of Gaussian03 and Crystal06 codes application to UN crystal in DFT calculation (the PW91 exchange-correlation functional [24]) with the use for U atom RECP SC60 [13] and the corresponding basis set, see [25] (with the removed diffuse functions, see Table 1). For the nitrogen atom the all electron basis set 6-311++G(2d,2p) [25] was used and the diffuse Gaussian function with the orbital exponent 0.0639 was removed. For UN lattice parameter \(a=4.88\ \text{Å}\) the total energy per unit cell of is -531.9863 a.u. (Crystal06) and -531.9873 a.u. (Gaussian03). The Mulliken atomic populations and the optimized lattice constant value are also close. In the further discussion we use the results of LCAO calculations by Crystal06 code for bulk solids as this code uses the point symmetry in the direct lattice and BZ summations. The cohesive energy calculation requires the free atom energy values for U and N atoms. As free atom BS includes diffuse GTF’s, the atomic energies were obtained by Gaussian03 code.

In Table 2 the results of bulk UN crystal calculation are presented for the three different RECPs mentioned in previous section. As it is seen from Table 2, the choice of RECP SC60 is preferable as giving the best agreement for the experimentally known properties of UN crystal. The calculated U atom charge \(Q_U\) is close to 1.6 in all the calculations while the populations of U atom d- and f-orbitals
are sensitive to RECP choice. However spin-density $SD = 1.06 \mu_B$ is the mostly close to the experimental value $0.85 \mu_B$ [26] for RECP SC60.

Table 3 presents the results of calculations with the RECP SC60 and different choices of the Hamiltonian of a crystal: unrestricted Hartree-Fock (UHF), DFT (PW91 [24], PBE [27]) and hybrid B3PW [28] and PBE0 [29].

Table 2. The results of LCAO calculations for UN crystal. The energy per unit cell $E_{\text{tot}}$ and the U atom energy $E_U$ are given in a.u., the cohesive energy $E_c$ in eV, the lattice constant in Å and the bulk modulus $B$ in GPa. The experimental values are given in brackets in the first column. The U-atom spin-density $SD$ is given in $\mu_B$.

| Property | MT78  | MT60  | SC60  |
|----------|-------|-------|-------|
| $a$ (4.89) | 5.17  | 4.78  | 4.80  |
| $E_{\text{tot}}$ | -106.5218 | -531.0228 | -531.9898 |
| $E_U$ | -51.5970 | -475.9572 | -476.9186 |
| $E_c$ (13.6) | 9.6 | 13.4 | 13.6 |
| $B$ (194) | 167.2 | 291.6 | 276.9 |
| $Q_U$ | 1.63  | 1.55  | 1.58  |
| SD | 3.18  | 1.18  | 1.06  |

Table 3. The results of UN crystal calculations with the RECP SC60 (all the figures are given in the same units as in the Table 2).

| Property | UHF | PW91 | PBE | B3PW | PBE0 |
|----------|-----|------|-----|------|------|
| $a$ (4.89) | 4.84 | 4.80 | 4.80 | 4.79 | 4.78 |
| $E_c$ (13.6) | 4.3 | 13.6 | 13.7 | 11.6 | 11.6 |
| $Q_U$ | 1.89 | 1.58 | 1.57 | 1.68 | 1.69 |
| SD | 1.29 | 1.06 | 1.06 | 1.08 | 1.09 |

Population, $e$

| Property | UHF | PW91 | PBE | B3PW | PBE0 |
|----------|-----|------|-----|------|------|
| U $s$ | 4.03 | 4.04 | 4.04 | 4.04 | 4.03 |
| $p$ | 12.24 | 12.15 | 12.16 | 12.13 | 12.14 |
| d | 11.90 | 11.96 | 11.97 | 11.95 | 11.98 |
| $f$ | 1.94 | 2.27 | 2.26 | 2.20 | 2.16 |
| N $s$ | 3.89 | 3.87 | 3.87 | 3.88 | 3.88 |
| $p$ | 4.93 | 4.64 | 4.64 | 4.73 | 4.74 |
| d | 0.06 | 0.07 | 0.06 | 0.07 | 0.07 |

From Table 3 it is seen that the cohesive energy is essentially underestimated in UHF and hybrid DFT-HF calculations, but is close to the experimental value in DFT calculations. In the latter the results for two different exchange-correlation functionals are close. As for the lattice parameter $a$, our LCAO DFT value 4.80 Å is not too different from those obtained in other DFT calculations: 4.86 Å - Plane Wave (PW), RECP PAW [7], 4.82 Å – PW RECP US [8], 4.90 Å – all-electron calculation with the numerical AO [12], 4.86 Å - FP LAPW [10].

In the next section we discuss our DFT (PW91) LCAO results for mononitride UN in the comparison with those for two other nitrides UN$_2$ and U$_2$N$_3$. 

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4. Electronic structure and chemical bonding in uranium nitrides

Table 4 presents the calculated properties of UN, UN₂ and U₂N₃ crystals—lattice parameters, cohesive energy and bulk modulus. Our LCAO DFT (PW91) RECP SC60 results are compared with those obtained in DFT (PW91) calculations [7], using PW basis and two different RECP 78 potentials for uranium core electrons—Projected Augmented waves (PAW) and Ultra Soft (US).

Table 4. Comparison of the lattice parameters \(a, c\) (Å), cohesive energy \(E_c\) (eV) and bulk modulus \(B\) (GPa) obtained in DFT PW (PAW, US [7]) and LCAO (SC60) calculations with the exchange-correlation potential PW91. (Experimental values are given in bold.)

| Property | UN | UN₂ | UN₃ | UN₂ Opt. b.s. |
|----------|----|-----|-----|---------------|
| \(a, c\) | 4.86 | 4.95 | 4.80 | 4.83 | 3.65, 5.80 | 3.74, 5.72 | 3.66, 5.60 | 5.26 | 5.26 |
| Exp.     | 4.89 |          | 4.80 | 3.70, 5.82 | 5.30 |
| \(E_c\)  | 14.7 | 12.3  | 13.6 | 14.2 | 36.3 | 30.1 | 34.6 | 21.5 | 17.9 | 20.9 |
| Exp.     | 13.6 |          |          |          |          |          |          |          |
| \(B\)    | 226 | 182 | 277 | 237 | 209 | 154 | 232 | 265 | 236 | 270 |
| Exp.     | 194 |          |          |          |          |          |          |          |

For UN crystal there are given also the results (SC60 opt.b.s) obtained with the U atom and N atom basis set optimization during the crystalline calculation. The initial uncontracted GTFs exponents (U:0.287(s), 0.144(p), 0.490(f) and N: 0.201(p)) correspond to the energy per unit cell \(E = -531.98984\) a.u. The optimized values of these exponents are 0.221(s), 0.120(p), 0.102(d), 0.423(f), 0.185(p) and correspond to the energy per unit cell \(E = -532.01277\) a.u. The optimization of basis set was done by both Powell and Hooke-Jeeves methods [20], the optimized exponent values are practically the same in both methods. Analyzing the results given in Table 4 one can make the following conclusions.

Use of the same U atom BS (with the removed diffuse exponents, see Table 1) for all the three crystals gives calculated properties in reasonable agreement with the results obtained in Plane Wave calculations. LCAO results agree better with the PW results in the calculations with PAW effective core potential. The basis set optimization in LCAO calculations improves the agreement of the lattice parameter and bulk modulus of UN crystal with the experimental data, the change of the cohesive energy due to BS optimization is small.

Table 5. Local properties of uranium nitrides electronic structure.

| Property | UN | UN₂ | UN₃ | UN₂ Opt. b.s. |
|----------|----|-----|-----|---------------|
| \(Q_U\) (LCAO) | 1.58 | 2.29 | 2.78 | 1.16 |
| \(Q_N\) (LCAO) | -1.58 | -1.55, -1.46 | -1.39 | -0.58 |
| \(Q_U\) (PAW) [7] | 1.66 | 2.08 | 2.48 |
| \(Q_N\) (PAW) [7] | -1.66 | -1.50, -1.34 | -1.24 |
| SD | 1.06 | 0.58 | 0.0 | 1.09 |
| Population, \(e\) | | | | |
| U | s | 4.04 | 4.02 | 4.02 | 4.06 |
| p | 12.15 | 11.97 | 11.73 | 11.88 |
| d | 11.96 | 11.45 | 11.32 | 12.45 |
| f | 2.27 | 2.27 | 2.15 | 2.45 |
| N | s | 3.87 | 3.90, 3.89 | 3.89 | 3.81 |
| p | 4.64 | 4.58, 4.53 | 4.45 | 4.30 |
| d | 0.07 | 0.07, 0.04 | 0.05 | 0.05 |

The LCAO approach is a natural way for a study of the chemical bonding in a crystal as it allows the extension to the periodic systems the procedures of the chemical bonding analysis developed in
quantum chemistry of molecules [15]. In Table 5 we present the results of the Mulliken population analysis application to three uranium nitrides under consideration: atomic charges of U and N atoms ($Q_U$ and $Q_N$), spin density (SD) on U atom and Mulliken populations of atomic orbitals. For the comparison the Bader effective atomic charges are given, calculated in [7] using PAW RECP78 and PW basis set. As is seen from Table 5 the calculated atomic effective charges $Q_U$ differ from the formal ionic charges +3, +4.5 and +6 in UN, U$_2$N$_3$ and UN$_2$ crystals, respectively. The mixed metallic-covalent chemical bonding is found both in LCAO and PW calculations of UN and U$_2$N$_3$ crystals, in agreement with discussions in previous theoretical and experimental studies of UN crystal. UN$_2$ crystal has the semiconducting nature, in agreement with the results of all electron calculations [12]. Our LCAO results for changes in effective charges as a function of decreasing U:N ratio (from UN to UN$_2$) confirm the conclusion [7] that the uranium charge increases while the nitrogen charge decreases. However, the Mulliken atomic charges for optimized BS give more covalent chemical bonding in UN crystal, as the optimization increases the basis delocalization (see discussion of Table 4). At the same time SD values demonstrate small changes with BS optimization.

The results for AO populations (which are not found in Bader analysis) allow to analyze the role of different U atom orbitals in chemical bonding when using RECP SC60 for valence configuration 5$s^2$5$p^6$5$d^{10}$6$s^2$6$p^6$5$f^7$. As is seen from Table 5, the sum of 5$s$ and 6$s$ orbitals populations is close to 4 in all the three crystals demonstrating their small participation in the chemical bonding. The f-orbitals population is close in UN and U$_2$N$_3$ crystals, but in UN$_2$ crystal f-electrons are more delocalized due to high value of the formal U valence. From UPS and XPS investigations of the core and valence levels of UN, 2.2 ± 0.5 electrons in the 5$f$ band near Fermi level have been derived [26]. This result agrees with our LCAO (2.27) and FP LAPW [10] (2.17) values for 5$f$ populations. It is seen that the change of local atomic arrangement decreases p- and d-orbital populations. This means larger participation of these orbitals in the chemical bonding with the increase of the formal U valence.

Figure 2. Energy bands of UN crystal (LCAO DFT/PW91 calculations, RECP SC60), the energies are given in a.u., solid and dotted lines correspond to the states with spin up and spin down, respectively.

Figure 2 shows the upper part of valence and lower part of the conduction energy bands for UN crystal (LCAO DFT-PW91 calculations with RECP SC60), the total spin projection $S_z=1/2$). The states of the two lowest three times degenerated and non-degenerate subbands are formed by U (p) and U(s)+N(s) atomic orbitals, respectively. The three times degenerated band around energy -0.10 a.u. is mixed U(f)+N(p) band, the nondegenerate occupied band near Fermi level is formed by U(f) states.
The unpaired electron occupies the higher states of the three degenerated U(d) band near the Fermi level.

As seen from Tables 2 and 5, SD value in the ground state of metallic UN and U$_2$N$_3$ crystals is close to 1 in the calculations with RECP 60. This result differs from that found in [11]: for different RECP’s 78 used in [11] the ground state with the spin projection 3/2 appeared to be more favorable (the three f-electrons with parallel spins occupy the states near the Fermi level [11]). Figure 1 demonstrates that use of RECP SC60 moves the nondegenerate U(f) band down changing the electron occupation of the band states near Fermi level and SD on U atom. RECP SC60 results agree better with the experimental conclusion [26] that U atom in UN crystal has a moment 0.75 $\mu_B$.

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