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Hartree–Fock ground-state properties for the group 1 alkali metals and the group 11 noble metals

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Abstract

In order to use wavefunction-based correlation methods in solids it is necessary to have reliable Hartree–Fock results for the infinite system of interest. Therefore we performed Hartree–Fock calculations for the group 1 alkali metals (Li to Cs) and group 11 noble metals (Cu, Ag and Au). We optimized a basis set of valence-double- ζ quality for the periodic system. For the lighter atoms all-electron basis sets are applied, whereas for the heavier atoms small-core pseudopotentials with the corresponding basis sets were used to deal with the scalar-relativistic effects. We determine the cohesive energy, the lattice constant and the bulk modulus of the systems at the Hartree–Fock level. We use the counterpoise correction for the free atom to minimize the basis set superposition error occurring for finite basis sets. The effects due to the counterpoise correction not only for the cohesive energy but also for the lattice structure and bulk modulus are discussed in detail.

1. Introduction

The simple metals of groups 1 and 11 were extensively studied with much success in the framework of density functional theory (DFT). It is claimed that for the simple metals a local density approximation (LDA) [1] or gradient corrected versions of the functional [2, 3] are good approaches, because in simple metals the electrons are delocalized and therefore can be well described by a homogeneous electron gas.

Despite the practical success, the implicit treatment of the exchange and the correlation effects in one joint functional prohibits the deeper understanding of the nature of correlation effects. For that, *ab initio* wavefunction-based correlation methods like the method of increments (for a review see [4]) are necessary. These rely on the Hartree–Fock (HF) ground-state properties of the solid, and therefore reliable Hartree–Fock calculations are necessary for the infinite systems. It is possible to perform such calculations with the program package CRYSTAL [5], which works with Gaussian-type basis sets centred at the atoms involved, in the solid. HF results are not only necessary for systematically improvable correlations methods.

Having reliable HF results at hand, one can discuss in comparison with the experiment how large the correlation contributions are for different ground-state properties.

Especially for metals, which are the topic of this paper, Hartree–Fock calculations for the infinite systems are not trivial. The first problem is the high requirements for the numerical thresholds set on the Coulomb and the exchange series, and for the k -point mesh in the reciprocal space to evaluate the ground-state energy. Due to the diminishing gap between occupied and virtual states a very dense k -mesh is necessary to smooth out the HF singularity occurring in the density of states. The second problem that arises is that due to the basis sets which have to be used for the crystal calculations. Due to the dense packing in solids, very diffuse basis functions, which are normally used and necessary for the free atoms, cause linear dependences and yield numerical instabilities when they are used for periodic systems. For that reason the standard basis sets available for computations in atoms or molecules have to be re-optimized for the infinite solid.

For calculating measurable ground-state properties like the cohesive energy it is necessary to subtract from the crystal bulk energy (per atom) the energy of the free atom computed with a basis set of equal quality. The error which occurs if the same basis sets are used for the free atom and the bound system and not ones of equal quality is called the basis set superposition error (BSSE) [6]. The correction of this error can be achieved with the counterpoise (CP) correction [7] or by adding extra diffuse functions to the crystal-optimized basis set when computing the energy of the free atom. We will compare both methods and discuss the influence on the cohesive energy as well as on the lattice constant and the bulk modulus.

In this paper we report on such computations performed for open-shell metals with one s valence electron, i.e., group 1 alkali metals and group 11 noble metals. For lithium, there are reliable data in the literature [8], but we would like to add these data to our results to give an overview of the whole 1 group. The same is true for copper and silver, where the bulk data have been published as small parts of otherwise different investigations [9–11].

The paper is organized as follows. In the next section we present the technical details and describe the crystal-optimized basis sets. The Hartree–Fock results for the cohesive energy, lattice constant, bulk modulus and the band structure are presented in section 3, where the influence of the BSSE is also discussed in detail. The conclusion and an outlook follow in section 4.

2. Technical details and optimized basis sets

2.1. Optimized basis sets

Both group 1 and group 11 metals condense in the solid forming a cubic lattice. Whereas all group 1 metals have a body-centred cubic (bcc) ground-state structure at ambient pressure, the noble metals condense in the face-centred (fcc) structure.

We perform our calculations with the program package CRYSTAL03 [5], which relies on Gaussian-type basis functions for the atoms forming the crystal. To achieve accurate results for metals, it is not sufficient to use the standard CRYSTAL thresholds for the evaluation of bielectronic Coulomb and exchange integrals. We increase them at least up to 10^{-10} (both for overlap and penetration depth thresholds); for overlap of exchange HF series the threshold is even 10^{-16} (for a detailed description of the thresholds consult the CRYSTAL03 manual [5]). The density of the reciprocal space k -point mesh is critical for metals due to the vanishing gap at the Fermi level. We chose a Pack–Monkhorst k -point mesh with an isotropic shrinking factor of 12 (i.e. 12 k -points along each of the three dimensions in reciprocal space) and for the Gilat k -point net (needed in conducting systems) a shrinking factor of 24. This choice corresponds to 413 k -points in the irreducible part of the Brillouin zone. The numerical accuracy due

to such a choice is below 10^{-4} Hartree. A even denser mesh would be possible, but for future applications, where the lattice symmetry can be reduced (e.g. when calculating elastic constants), it is not recommended as such calculations would quickly overwhelm the resources of the computer. Still another accuracy requirement is to use the CRYSTAL option FIXINDEX which assures scaled cut-off parameters for different lattice constants (i.e. the same number of bielectronic integrals of the same type is evaluated for each separate computation).

However, the largest effort involved in these calculations is to determine a basis set which is suitable for the crystal calculations. Only for Li is a crystal-optimized basis set available [8]. For Na we started from the Dunning all-electron basis set [12] optimized for the free atom. All-electron basis sets are not practical for heavier atoms: K, Rb and Cs. Thus, we selected scalar-relativistic 9-valence-electron pseudopotentials [13] to describe their inner core electrons. (Note that f-projectors in the pseudopotentials are not possible in CRYSTAL03, therefore they are neglected. The influence on the total energy is small, because no valence f-shells are occupied.) For the corresponding valence-electron basis sets we needed a proper optimization. Namely, we started with standard basis sets from [14] and re-optimized the outer two exponents of each shell by minimizing the total crystal energy obtained with CRYSTAL03. We proceeded similarly for the group 11 solids. For the noble metals Cu, Ag and Au the scalar-relativistic 19-valence-electron pseudopotentials [15] are available together with Dunning-type basis sets [16].

As already mentioned, all basis sets suitable for free atoms and molecules have to be modified to be used in a crystal. The inner contractions of the atomic orbitals are kept unchanged, because the inner electronic shells in free atoms will not be very different from those in the solid. On the other hand the very diffuse outer exponents, which are necessary for the free atoms, must be neglected in the solid, because, due to the dense packing in the solid, basis functions on the neighbouring atoms will take over their part (i.e. any diffuse orbital on a particular atom can be, to some extent, reconstructed by using many orbitals centred at the multitude of the neighbouring atoms). Thus, in the bulk, we omit all exponents of the free-atom basis set which are smaller than 0.1 for the alkali metals and smaller than 0.2 for the noble metals and optimize in that region at least one exponent for each angular momentum separately. Concerning the exponents which were taken without any change from free-atom basis we keep their contraction coefficients without modification. In some cases only the number of contracted primitive functions is changed (i.e. some smaller exponents are decontracted to allow for more freedom for the description of both the inner shells and the outer shells). For Rb and Cs we also optimized an inner d exponent, because in these metals the hybridization of the occupied valence s shell to the unoccupied p and d shells is about of equal strength. The resulting basis sets are summarized in tables 1, 2 and 3.

2.2. Basis set superposition errors

When calculating the cohesive energy of the crystal it is important that the atom in the bulk and the free atom (the calculations for the free atoms are performed with the program package MOLPRO³) are described with basis sets of equal quality. That does not mean the same basis set, because extra diffuse functions are necessary for the proper description of a free atom whereas in solid they are not needed as such diffuse functions centred on a particular atom are mimicked by the presence of orbitals centred on neighbouring atoms. The error which would

³ MOLPRO version 2002.6 — a package of *ab initio* programs written by H-J Werner and P J Knowles with contributions from J Almlöf, R D Amos, A Bernhardsson, A Berning, P Celani, D L Cooper, M J O Deegan, A J Dobbyn, F Eckert, C Hampel, G Hetzer, T Korona, R Lindh, A W Lloyd, S J McNicholas, F R Manby, W Meyer, M E Mura, A Nicklass, P Palmieri, R Pitzer, G Rauhut, M Schütz, H Stoll, A J Stone, R Tarroni and T Thorsteinsson.

Table 1. The optimized all-electron crystal-basis set of valence-double- ζ quality for the Na metal in the bcc structure. The (2s2p1d) functions are optimized for the crystal.

Na	Exp.	Coeff.	Coeff.
s	31 700.0	0.000 46	-0.000 11
	4755.0	0.003 55	-0.000 87
	1082.0	0.018 26	-0.004 51
	306.4	0.071 67	-0.018 14
	99.53	0.212 35	-0.058 08
	35.42	0.416 20	-0.137 65
	13.30	0.373 02	-0.193 91
	4.392	0.062 51	0.085 80
	1.676	-0.006 25	0.604 42
		0.59	1.000 00
	0.08	1.000 00	
p	138.1	0.005 80	
	32.24	0.041 58	
	9.985	0.162 87	
	3.484	0.359 40	
	1.231	0.449 99	
		0.42	1.000 00
	0.08	1.000 00	
d	0.10	1.000 00	

occur if one uses exactly the same basis sets in the crystal and in the free atom is called the basis set superposition error (BSSE) [6]. Two possibilities are used to correct for the BSSE. In particular, for crystal calculations a widely used method is to use the optimized crystal basis set with a set of additional diffuse functions for the free atom. For this aim we have selected for the group 1 elements an extra common sp diffuse exponent (Li: 0.04, Na to Cs: 0.02) and for the group 11 elements a common spd exponent (0.05).

Another possibility to overcome the BSSE is the so-called counterpoise correction (CP) [7]. This is mainly used for molecules when calculating their dissociation curve. For the CP correction we do not supplement the single free atom by additional diffuse exponents. Instead we use the same basis set as the one used in the CRYSTAL computations. However, the atom considered is surrounded by so-called ghost atoms. The ghost atoms have no charge, neither any electrons. They are simply a shell of geometrical centres placed at the same positions as the corresponding atoms in solid. Each centre is equipped with the crystal-optimized basis set. The CP correction is in contrast to the first approach dependent on the lattice constant, because the free-atom energy varies when the distance of the ghost basis sets placed in the surroundings (see figure 1) is varied.

When changing the lattice constant by 1 Å around the experimental lattice constant the free-atom energy changes typically by about 0.01 au, which corresponds to 7% of the cohesive energy. Because the atomic energy decreases in magnitude with the increasing lattice constant, the CP-calculated lattice constant will be larger than the one obtained by the first method, i.e. where we use the fixed additional diffuse exponent, which yields a distance-independent atomic energy. Which approach for the BSSE corrections is more reasonable when calculating the lattice constant of the bulk metal will be discussed in detail in the next section.

There are some practical considerations with respect to the CP method. Namely, for a crystal the CP correction depends on the number of ghost atoms that are used. The limit of

Table 2. The optimized crystal-basis sets of at least valence-triple- ζ quality for the alkali metals K, Rb and Cs for the corresponding scalar-relativistic 9-valence-electron pseudopotentials. (Exception: the p-shell for Cs converges only in valence-double- ζ quality.) The basis sets are named after the pseudopotentials. The optimization for the two outermost exponents of each shell (exception three outermost d exponents for Rb and Cs) is performed in the bcc structure.

ECP	K		Rb		Cs	
	ecp10mwb		ecp28mwb		ecp46mwb	
	Exp.	Coeff.	Exp.	Coeff.	Exp.	Coeff.
s	31 478.746	0.003 98	4.668 7885	0.290 08	5.877 8113	0.128 59
	4726.8876	0.030 50	2.944 2428	-0.677 40	4.363 1538	-0.346 32
	1075.4345	0.150 73	0.581 7126	0.457 12	1.804 8475	0.699 30
	303.398 11	0.519 12				
	98.327 112	1.036 69				
	33.636 222	0.763 98				
s	65.639 209	-0.282 42	0.451 4793	1.000 00	0.374 8523	1.000 00
	7.316 2592	1.691 49				
	2.890 2580	1.296 53				
s	4.545 9748	-0.007 63	0.216 0492	1.000 00	0.163 8485	1.000 00
	0.704 0412	0.025 63				
	0.282 6688	0.016 60				
s	0.25	1.000 00	0.06	1.000 00	0.07	1.000 00
s	0.05	1.000 00				
p	361.224 92	0.020 90	4.668 7885	0.290 08	4.275 1856	0.045 72
	84.670 222	0.150 43	2.944 2428	-0.677 40	1.965 6663	-0.250 19
	26.469 088	0.554 40	0.581 7126	0.457 12	0.476 8919	0.556 60
	9.265 8077	1.040 90				
	3.342 3388	0.678 25				
p	1.510 0876	0.752 48	0.330 880 71	1.000 00	0.215 2974	1.000 00
	0.565 6837	1.370 85				
	0.208 1700	0.660 47				
p	0.25	1.000 00	0.18	1.000 00	0.07	1.000 00
p	0.05	1.000 00	0.06	1.000 00		
d	0.353	1.000 00	0.45	1.000 00	0.215	1.000 00
	0.098	1.000 00	0.12	1.000 00	0.133	1.000 00
			0.06	1.000 00	0.07	1.000 00

infinite number, which corresponds to the whole crystal lattice, is not possible. Only a finite number of ghost atoms can be tackled. Our choice is to take 14 ghost atoms for the bcc lattice (equipped with full crystal basis set each) or even more, i.e., 26 atoms (d-exponents omitted for the outer 12 atoms), where we see apparently no difference. For the fcc lattice (group 11 metals) with the filled d shell the d exponent should not be omitted; therefore, we select a smaller surrounding of 18 atoms.

For gold, we have tested the different approaches and different numbers of surrounding dummy atoms (see table 4). The difference between the pure crystal basis set and the optimized atomic basis set for the single free Au atom is 0.0547 au, which corresponds to about 40% of the cohesive energy of the Au metal in the fcc structure. This large error is of course not tolerable. If we use the CP corrections with only 12 nearest-neighbour ghost atoms the atomic energy decreases drastically, and the difference from the optimized atomic basis set is about 0.01 au,

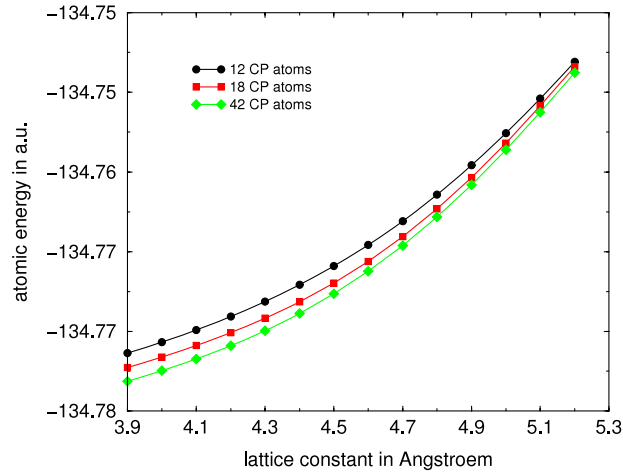


Figure 1. The dependence of the CP corrected ground-state energy of the free Au atom on the lattice constant. Different surroundings are plotted.

(This figure is in colour only in the electronic version)

Table 3. The optimized crystal-basis sets of valence-triple- ζ quality for noble metals or the corresponding scalar-relativistic 19-valence-electron pseudopotentials. The basis sets are named after the pseudopotentials. The optimization for the two outermost exponents of each shell (with the exception of the three outermost spd exponents for Au) is performed in the fcc structure.

ECP	Cu			Ag			Au		
	Exp.	eep10mdf		Exp.	eep28mdf		Exp.	eep60mdf	
		Coeff.	Coeff.		Coeff.	Coeff.		Coeff.	Coeff.
s	560.088	0.000 64	-0.000 14	180.075	0.000 85	-0.000 20	38.000 80	0.020 01	-0.005 30
	56.6486	-0.009 74	0.001 40	21.8987	-0.065 45	0.015 72	23.972 50	-0.151 68	0.046 32
	35.4258	0.065 79	-0.013 17	13.8670	0.297 77	-0.079 23	15.218 20	0.363 96	-0.119 94
	11.0546	-0.415 04	0.095 70	6.1426	-0.753 12	0.222 63	5.539 99	-0.821 33	0.304 06
	2.306 82	0.746 61	-0.211 87	1.438 14	0.881 18	-0.349 20	1.385 51	0.936 64	-0.494 50
s	0.951 43	1.000 00		0.648 382	1.000 00		0.64	1.000 00	
	0.18	1.000 00		0.15	1.000 00		0.16	1.000 00	
p	70.9739	0.003 68		11.875 10	0.116 25		10.309 20	0.128 22	
	17.8510	-0.082 13		8.002 450	-0.307 29		6.627 65	-0.353 79	
	4.246 79	0.375 38		2.017 660	0.515 74		1.674 47	0.566 21	
	1.877 60	0.508 41		0.954 230	0.503 10		0.801 11	0.493 17	
p	0.793 34	1.000 00		0.423 118	1.000 00		0.50	1.000 00	
	0.18	1.000 00		0.19	1.000 00		0.18	1.000 00	
d	60.3804	0.017 56		26.432 00	0.003 48		11.002 70	0.016 47	
	19.1121	0.099 13		11.034 50	-0.013 85		6.891 66	-0.068 01	
	6.952 88	0.271 17		2.737 870	0.254 60		1.808 08	0.299 49	
	2.609 94	0.406 18		1.195 750	0.449 85		0.821 05	0.454 30	
d	0.922 57	1.000 00		0.482 042	1.000 00		0.45	1.000 00	
	0.283 64	1.000 00		0.18	1.000 00		0.18	1.000 00	

Table 4. The ground-state energy in au of the free Au atom with different basis sets.

Au	(au)
Crystal basis set	-134.72495775
CP of 12 atoms	-134.76991847
CP of 18 atoms	-134.77089195
CP of 42 atoms	-134.77173293
+ 1s1p1d	-134.76925167
Opt. atomic basis (VDZ)	-134.77960928

and therefore by a factor of 5 smaller. About the same value is achieved with the crystal-basis set with additional diffuse spd functions. The difference we notice when using a shell of 12 atoms or 18 atoms is 0.001 au, and therefore small compared to the difference between CP-corrected and additional diffuse functions. The difference when using the shell of 42 atoms and the optimized atomic basis set is 0.0077 au, about 6% of the cohesive energy. That is the error which is caused due to the finite basis set on the atom and the crystal, although both are optimized, it is not clear whether they are really balanced for the calculation of the cohesive energy. Therefore we have to regard an error of about 6% of the cohesive energy due to the use of basis sets of different quality for the bulk and the free atom.

3. Results and discussion

The experimental data (i.e. lattice constants, cohesive energies, bulk moduli) we used for comparison with our data were taken from the CRC handbook of Chemistry and Physics [17], and also from [18–20]. The computed cohesive energies are corrected by the phononic zero-point energy calculated in the Debye approximation [21]. The Debye temperature was taken from [18]. For elements where reliable lattice constants at zero temperature were not available we extra/-polated the lattice constant as measured at a finite temperature to zero kelvin by using a thermal linear expansion coefficient taken from [17].

3.1. Lattice constant

The lattice constant of a cubic crystal is normally evaluated as the minimum of the total energy curve, calculated with a special approximation of the Hamiltonian. We focus here on the Hartree–Fock approximation and calculate the HF ground-state energy versus the lattice constant. The optimized lattice constants of the total energy for the group 1 and group 11 metals are listed in the first column of table 5. The lattice constants corrected by the CP corrections are listed in the second column of table 5. If one compares the two values, one realizes that the difference between the two values can be up to 0.35 Å (for Cs), which corresponds to 6% of the experimental lattice constant. The deviation between the lattice constant as obtained by using the total energy and by using the CP corrected one increases for heavier atoms in group 1. There the CP correction has a strong influence on the lattice constant, probably because the basis sets for the heavier atoms compared to the basis set for lighter elements are of poorer quality. In particular, for Cs the influence of the CP correction is large. The density of states for bulk Cs around the Fermi level is not only a mixture of s and p character, but also the d-functions are of equal importance at the Fermi level. Note that the lowest unoccupied band is predominantly of d character. This spd hybridization causes various structural phase transitions for Cs under pressure [22], and therefore Cs is a very special alkali metal, and electronic correlations will play an important role.

Table 5. The HF and LDA lattice constant in Å, calculated with the total energy and with the CP-corrected cohesive energy in comparison with the experimental lattice constant.

a (Å)	HF	HF	LDA	Exp.
	from tot. en.	from CP coh. en.	from tot. en.	
bcc Li	3.65	3.73	3.36	3.49
bcc Na	4.42	4.57	4.05	4.23
bcc K	5.62	5.85	5.05	5.23
bcc Rb	5.98	6.27	5.40	5.59
bcc Cs	6.06	6.41	5.60	6.05
fcc Cu	3.89	4.06	3.52	3.60
fcc Ag	4.38	4.49	4.01	4.06
fcc Au	4.31	4.36	4.08	4.06

For the group 11 metals, the difference between the total energy minimum and CP-corrected one are smaller (largest for Cu). That can be explained by the occupied d shell, which, by the way, contributes significantly to the correlation energy. We have regarded in solid mercury, that the valence s correlations only do not bind the solid [23, 24]. Coming back to the filled d shell, we note that due to its compactness, it is not so dependent on the CP correction as the more extended valence s shell. For the same reason the relativistic contraction of the valence s shell of Au reduces the effect of the CP correction of Au compared to Ag and Cu.

If we compare our results to the experimental values, the HF lattice constants are too large for all examined group 1 and group 11 metals. Overall one has to admit that accurate results for lattice constants are difficult to obtain with the HF method. It is not obvious whether the calculation of the lattice constant from the total energy curve or the energy curve with the CP correction is more correct. Only computations employing significantly better basis sets can bring a solution to this problem, but at present they are not possible with the CRYSTAL code. The two values given in table 5 give the upper (CP-corrected) and lower bound (from total energy) of the lattice constant and therefore are a good measure of the error due to a chosen basis set.

To test the quality of our basis set (i.e. the one we optimized for the solid), we performed DFT calculations for the solid with an LDA functional (SVWN functional [25]). As expected for the LDA functionals the lattice constants are too small for the alkali metals, and they agree well with the experimental ones for the noble metals. We can compare our results obtained with Gaussian-type basis sets with similar results obtained when using the plane-wave LDA, e.g. for Li [26] (3.36 Å) or for the noble metals [27] (Cu: 3.52 Å, Ag: 4.01 Å, Au: 4.06 Å) and for Cs [28] (5.79 Å). For the lighter alkali metals and the noble metals there is a good agreement between the Gaussian-type basis and the plane-wave basis results. Only for Cs is the difference not negligible. That gives a clear hint that probably the quality of the optimized Gaussian basis set for Cs (which is the best-quality basis set which still gives HF convergence in CRYSTAL), is not sufficient. Although the HF lattice constant of Cs obtained from optimizing the total energy is in good agreement with the experiment, the large influence of the CP correction shows that this agreement is coincidental.

3.2. Cohesive energy

The cohesive energy of the solid, defined as the difference between the total energy and the energy of the single free atom, was calculated for the experimental lattice constant as well as for the HF minimum. For the first case we compare the values where the free-atom energy is

Table 6. The HF cohesive energy in eV calculated when for the single free atom additional diffuse functions were used or when the CP correction was used. In the first two columns the cohesive energy is evaluated at the experimental lattice constant, and in the third column it is evaluated at the HF minimum.

E_{coh} (eV)	At exp. latt.		At min. latt.	
	Atom + dif. func	Atom CP corr.	Atom CP corr.	Exp.
bcc Li	-0.51	-0.52	-0.55	-1.65
bcc Na	-0.21	-0.18	-0.23	-1.15
bcc K	-0.09	-0.04	-0.14	-0.95
bcc Rb	+0.06	+0.04	-0.08	-0.86
bcc Cs	+0.28	+0.10	+0.04	-0.81
fcc Cu	-0.59	-0.67	-1.00	-3.52
fcc Ag	-0.41	-0.47	-0.79	-2.97
fcc Au	-0.85	-0.80	-1.10	-3.83

calculated using additional diffuse functions and thus the cohesive energy is not dependent on the lattice constant and when the free-atom energy is calculated using the CP correction. The results are listed in table 6. In comparison with the experiment the HF cohesive energy is at most one third of the experimental value. Even for the alkali metals a significant part of the binding is due to correlations. For the heavier group 1 metals the HF cohesive energy is even repulsive. That fact is in a good correspondence with the large deviations of the lattice constant discussed in the previous section. The deviation between the cohesive energy as obtained using the single-atom energy with extra diffuse functions and cohesive energy when using the CP correction is at most 8% of the experimental cohesive energy with the exception of Cs. The difference between the cohesive energy at the experimental lattice constant and the optimized HF lattice constant is for the group 1 metals at most 0.1 eV and therefore in the range of 10% of the experimental value. Although the differences in the lattice constants are large, due to the small curvature of the total energy curve (i.e. small bulk modulus, see next section) the effect on the cohesive energy change is small. That is different in the case of the noble metals. Due to their high bulk modulus, the shift in the cohesive energy from the experimental to the HF minimum lattice constant is about 0.3 eV. But due to the larger experimental cohesive energy it also corresponds to about 10% of the experimental value.

3.3. Bulk modulus

The bulk modulus of a cubic lattice can be directly evaluated from the $E_{\text{coh}}(a)$ curve. As an example the $E_{\text{coh}}(a)$ curve is plotted for Au in figure 2. One can see in figure 2 that the cohesive energy is positive for lattice constants larger than 5 Å. This effect is correct in the HF treatment. Conceptually, the HF method cannot describe the correct dissociation limit, which would correspond to a zero cohesive energy at infinite distances of the atom as the HF method cannot describe the dissociation limit of the H_2 molecule. The CP-corrected curve for a larger lattice constant is still binding, which suggests that it can give the dissociation limit from experiment, but not the correct one in the approximation (HF) applied. Which treatment is better in the region of the minimum of the curve can be not decided *a priori*.

For the fcc lattice, with four atoms per unit cell volume, the expression is

$$B = \left(\frac{4}{9a} \frac{\partial^2}{\partial a^2} - \frac{8}{9a^2} \frac{\partial}{\partial a} \right) E_{\text{coh}}(a). \quad (1)$$

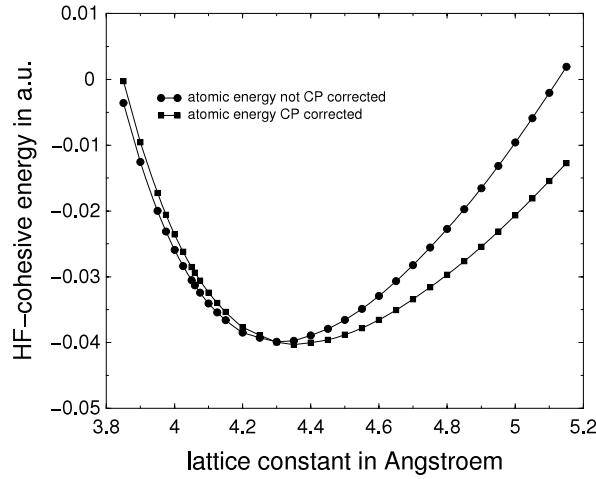


Figure 2. The cohesive energy curve with respect to the lattice constant of Au. For the circles the atomic energy is not lattice constant dependent, for the diamonds the ground-state energy of the free atom is calculated with the CP correction.

Table 7. The HF bulk modulus in Mbar calculated, where for the free atom additional diffuse functions are used or where the CP correction is used. In the first two columns the bulk modulus is evaluated at the experimental lattice constant, and in the third and fourth column it is evaluated at the HF-optimized lattice constant.

B (Mbar)	At exp. latt.		At min. latt.		Exp.
	Atom + dif. func	Atom CP corr.	Atom + dif. func	Atom CP corr.	
bcc Li	17.4	16.2	11.9	8.1	13.0
bcc Na	11.0	9.9	8.2	5.4	6.3
bcc K	6.3	6.4	3.4	2.4	3.1
bcc Rb	6.0	5.5	5.5	2.6	2.5
bcc Cs	7.2	5.8	7.2	4.6	1.6
fcc Cu	174	158	77	32	140
fcc Ag	151	147	61	36	100
fcc Au	229	227	100	78	220

For the bcc lattice, with two atoms per unit cell volume, the expression is

$$B = \left(\frac{2}{9a} \frac{\partial^2}{\partial a^2} - \frac{4}{9a^2} \frac{\partial}{\partial a} \right) E_{\text{coh}}(a). \quad (2)$$

If we evaluate the bulk modulus at the HF level at the experimental lattice constant, the second term in (1) and (2) is non-zero. To see the influence of this term and also the influence of the CP correction on the bulk modulus we have listed in table 7 the HF bulk modulus as evaluated at the HF-optimized lattice constant and at the experimental one, both determined from the total energy curve and from the CP-corrected cohesive energy curve. The bulk modulus was extracted from a quartic fit in the case of noble metals and a cubic fit in the case of alkali metals. The bulk modulus of the noble metals is on average by a factor of 20 larger than the bulk modulus in the alkali metals. We have to discuss two different effects on the bulk modulus. If we calculate the bulk modulus as evaluated at the HF minimum lattice constant, which is far too large compared to experiment, one would expect a too small bulk modulus. That is the case for the lighter alkali metals and for the noble metals. On the other hand, when evaluating the

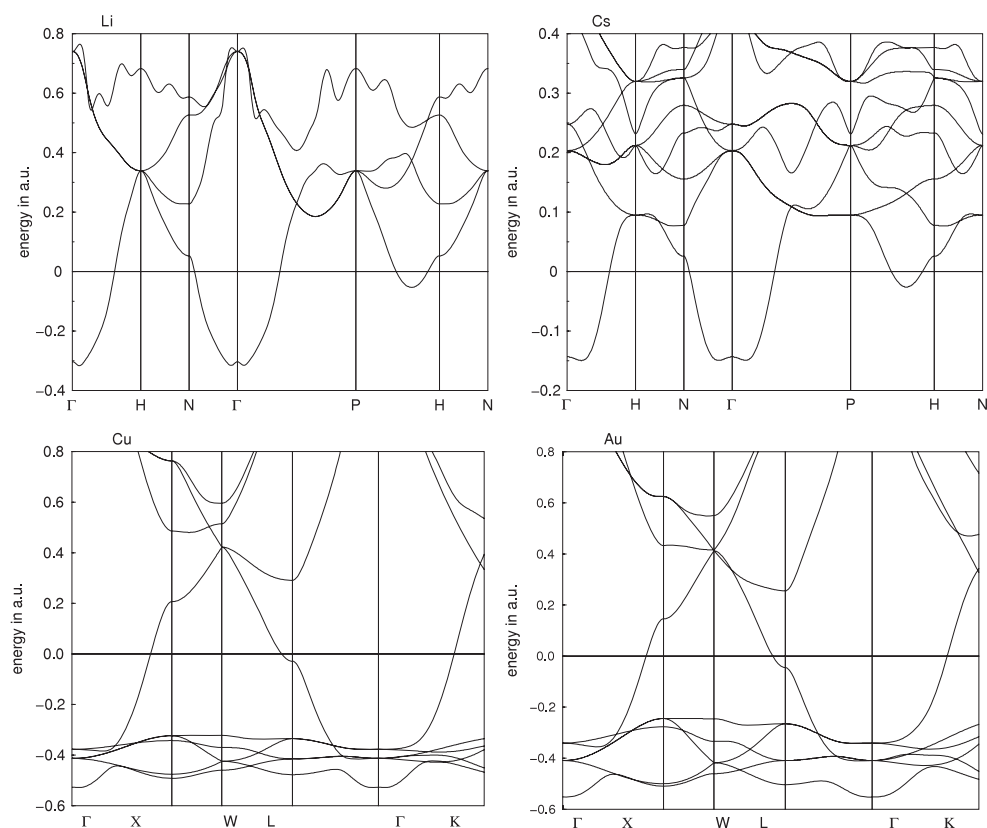


Figure 3. The HF band structure of Li, Cs, Cu and Au in selected directions of the Brillouin zone. The energy axis is in au; the small wiggles at the Γ point are of numerical origin due to the finite k -mesh used in the computation.

bulk modulus at the experimental lattice constant, the bulk modulus is too high compared to experiment. This is so because electronic correlations in true crystals reduce the bulk modulus due to the instantaneous reaction of the electrons to a static pressure. The influence of the CP correction on the bulk modulus is larger at the optimized HF lattice constant. The much too high HF bulk modulus of Cs again gives a hint that Cs is special for the group 1 metals due to the large spd hybridization.

All these considerations show that it is difficult to achieve accurate results for the HF bulk modulus, if the calculated lattice constant is not in good agreement with the experiment. That can be only achieved if the basis set is of such a good quality that the influence of the CP correction on the ground-state properties is small.

3.4. Band structure

For each of the studied metals the HF energy bands and density of states were computed at the experimental lattice constant. The band structure for Li and Cs and for Cu and Au are plotted in figure 3. They show distinct similarities. Namely, the s band of valence electrons loses (when crossing the Fermi energy level) its s-type character. For the lighter alkali metals like lithium, and for the noble metals, where the d shell is filled, the character changes to p-like, whereas for

the heavier alkali metals, where the d shell is unoccupied and overlapping with the p, we get a mixing of p and d. Whereas the valence s band which is crossing the Fermi level is very similar in Cu and Au, the decontraction of the occupied d shell is observed in a broadening of the d band by about a factor of 2 when comparing Cu and Au. The valence HF band structure and the conduction bands around the Fermi level are quite similar to the ones obtained with DFT methods (e.g. see [29]). For the higher-lying conduction bands significant discrepancies occur due to the limited basis set used in both approaches. But it is in general not expected for any ground-state method like HF that higher-lying bands can be reasonably described.

4. Conclusion

We have presented HF calculations for the ground-state properties of alkali and noble metals. Overall the cohesive energy is below 30% of the experimental value, so a subsequent correlation treatment is necessary to describe the ground-state properties in good agreement with experiments. First attempts have been made in our group to use an the local incremental expansion for the computation of the correlation energy of metals [23, 24, 30, 31]. In the case of mercury, where at the HF level the solid is not bound at all, when including the correlations at a coupled cluster level we achieved a very good agreement with the experiment for the cohesive energy [23], and also for the lattice structure and the bulk modulus [24]. The same is true for magnesium [31].

Whereas the correlation calculations are highly accurate and can be improved systematically, the question of the accuracy of the Hartree–Fock values arises: one source of a possible inaccuracy of the HF ground-state properties is the calculation of the energy of the free atom, which is necessary to calculate the cohesive energy in the solid. It can be calculated with the crystal basis with extra diffuse functions or using the CP method, where the atomic energy is lattice constant dependent. The differences in the cohesive energy between both methods are at most 8% of the experimental cohesive energy. The deviations in the determined lattice constant can be up to 0.35 Å for the heavier elements, which corresponds to a deviation from experiment by up to 6%. A better agreement can only be achieved with better Gaussian basis sets both for the solid and the atom. But with the present version of CRYSTAL that is not possible for metals. Therefore we have to regard the two different values of the lattice constant we obtained as upper (with CP correction) and lower (from the total energy) bounds.

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