

Theoretical study of the cohesive and structural properties of Mo and W in bcc, fcc, and hcp structures

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The structural properties of Mo and W in the bcc, fcc, and hcp structures are calculated using a fully-self-consistent pseudopotential linear combination of atomic orbitals method. Equilibrium lattice constants, cohesive energies, bulk moduli, differences in structural energies, and Mulliken-population analyses are obtained. For both elements, the bcc structure is found to be the most stable while the fcc and hcp structures have very similar cohesive energies. We find that the difference in the sum of eigenvalues gives the correct sign but not the magnitude for the difference in total energy between the bcc and fcc structures.

I. INTRODUCTION

The local-density approximation (LDA) within the density-functional formalism¹ has in recent years been very successful in determining the structural properties of a large variety of materials.^{2,3} Within LDA, a number of first-principles calculation schemes have been developed. These methods are usually more suitable for one type of material than others. For example, for simple metals and semiconductors, ground-state and structural properties can be calculated accurately and efficiently with the plane-wave method together with the pseudopotential formalism.^{2,3} On the other hand, transition elements in close-packed structures are more often treated by methods like Korringa-Kohn-Rostoker (KKR),^{4,5} linear muffin-tin orbital (LMTO),⁶ full-potential linear-augmented-plane-wave (FLAPW),⁷ self-consistent local-orbital (SCLO),⁸ and the mixed-basis approach.⁹ It is desirable to have a method of general applicability such that different systems can be calculated with approximately the same amount of effort to the same level of accuracy. This will be important in the long run for more complicated materials that may contain elements of very different characters. A recently developed pseudopotential LCAO scheme¹⁰⁻¹² could prove to be in this category. Applications of this method to the ground-state and structural properties of insulators and semiconductors have been reported.¹³⁻¹⁷ In the present paper we report the computation of structural properties of Mo in the 4*d* and W in the 5*d* transition series.

Transition metals have been an area of keen theoretical interest, not only because they are of important technological use, but also because they exhibit many interesting physical properties. An example is the (hcp→bcc→hcp→fcc) structural pattern across the *d* series as the *d* bands are filled progressively. In recent years, Mo and W have assumed the stature of "prototypical" transition met-

als and have been used as testing grounds for electronic and total-energy calculations. Their structural properties in the ground-state bcc phase have been studied by various authors.^{5,18-23}

The structural properties of Mo and W are very similar. We found that for both elements the bcc structure is the most stable and the calculated ground-state structural properties such as lattice constants and bulk moduli agree favorably with experiments. The fcc and hcp structures are very close in energy at the volumes considered. At equilibrium, they are about $\frac{1}{2}$ eV smaller in cohesive energy than the bcc structure. The equilibrium volume of the bcc structure is about 1-2% smaller than those of the fcc and hcp structures. The bulk moduli at equilibrium for the different structures have very similar values.

The remainder of the paper is arranged as follows. The fully-self-consistent pseudopotential LCAO method is reviewed in Sec. II. In Sec. III the total-energy results of the present calculations are presented. Section IV is a discussion and summary.

II. METHOD

In the present calculations, a Hamann-Schlüter-Chiang-type pseudopotential²⁴ was used for Mo and a scalar-relativistic norm-conserving pseudopotential²⁵ was used for the heavier W. The ionic pseudopotentials are taken (up to $l=2$) to be

$$V_{\text{ion}}(\mathbf{r}) = V_d(\mathbf{r}) + \sum_{l=0}^1 [V_l(r) - V_d(r)] |l\rangle\langle l|, \quad (1)$$

i.e., $V_s - V_d$ and $V_p - V_d$ are used as the nonlocal components. Atomic pseudocharge densities are superimposed to form an approximate crystalline charge density $[\bar{\rho}(\mathbf{r})]$ from which the initial Hartree (V_H) and exchange-correlation (V_{xc}) potentials are generated. These poten-

tials are decomposed into a linear combination of atomic effective electron screening potentials which are added to the bare ionic d pseudopotential to form a neutral local potential for each atom:

$$V_{\text{loc}}(\mathbf{r}) = V_d(\mathbf{r}) + V_H^{\text{eff}}(\bar{\rho}, \mathbf{r}) + V_{\text{xc}}^{\text{eff}}(\bar{\rho}, \mathbf{r}). \quad (2)$$

Since the superposition of atomic charge density $\bar{\rho}(\mathbf{r})$ is usually not far away from the self-consistent charge in the crystal, a construction like Eq. (2) gives a very reasonable starting potential for the self-consistency cycles. Both the local (V_{loc}) and nonlocal ($V_l - V_d$) potentials are short ranged and they are fitted to Gaussian expansions of the form

$$V(\mathbf{r}) = \sum_i c_i e^{-\beta_i r^2}. \quad (3)$$

This representation allows the use of analytic three-center integrals in the Hamiltonian matrix elements. An accurate fitting of the potentials is done by a Monte Carlo simulated annealing scheme.²⁶ Fitted values of c_i and β_i are tabulated in Table I for both Mo and W.

The wave functions are expanded in a LCAO basis set $\{\phi_i\}$ which has the form

$$\phi_i(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot (\mathbf{R} + \boldsymbol{\tau}_\mu)} f_{alm}(\mathbf{r} - \mathbf{R} - \boldsymbol{\tau}_\mu), \quad (4)$$

where $i = \{lm\mu\alpha\}$ here is a composite index, Ω is the crystal volume, \mathbf{R} is a lattice vector, $\boldsymbol{\tau}_\mu$ is a basis vector, and $f(\mathbf{r})$ are localized functions of the form

$$f_{alm}(\mathbf{r}) = A_{alm} r^l e^{-\alpha r^2} K_{lm}(\theta, \phi), \quad (5)$$

where the A 's are normalization constants. "Kubic harmonics" (K_{lm}) up to $l=2$ (i.e., s, p, d states) are included. Four decay constants (α) are used for the radial function for Mo and W. They are listed in Table II and are chosen to minimize the total energy of the system. The Hamiltonian matrix sizes are 40×40 for the bcc and fcc structures and 80×80 for the hcp structure, which has two atoms in the unit cell.

The calculations are carried to full self-consistency with a momentum-space self-consistency scheme that has been reported elsewhere.¹² Fourier components of the overlap matrices, $\pi_{ij}(\mathbf{k}, \mathbf{G})$, are evaluated:

$$\pi_{ij}(\mathbf{k}, \mathbf{G}) = \left\langle \mathbf{k}, j \left| \frac{e^{-i\mathbf{G} \cdot \mathbf{r}}}{\Omega_c} \right| \mathbf{k}, i \right\rangle, \quad (6)$$

where Ω_c is the volume of the unit cell, \mathbf{G} are reciprocal-lattice vectors, and $|\mathbf{k}, i\rangle$ are the basis orbitals. These overlap matrices are used directly to compute the charge density ρ (and hence the total energy), and the changes of the Hamiltonian matrix elements at a \mathbf{k} point, $\delta H(\mathbf{k})$, for an arbitrary change in the crystal potential δV (and hence can be used to update the Hamiltonian matrices as the potentials change during the iteration procedure):

$$\rho(\mathbf{G}) = \sum_{n, \mathbf{k}} \psi_{n\mathbf{k}}^\dagger \pi(\mathbf{k}, \mathbf{G}) \psi_{n\mathbf{k}} \quad (7)$$

and

$$\delta H_{ij}(\mathbf{k}) = \sum_{\mathbf{G}} \delta V(\mathbf{G}) \pi_{ij}^*(\mathbf{k}, \mathbf{G}) \Omega_c. \quad (8)$$

Matrix notation is used in Eq. (7) and $\psi_{n\mathbf{k}}$ is the eigenvec-

TABLE I. Coefficients (c_i), in Ry, and exponential decays (β_i), in a.u.⁻², for the Gaussian expansions of local and nonlocal potentials for Mo and W.

V_{loc}		$V_p - V_d$		$V_s - V_d$	
β_i	c_i	β_i	c_i	β_i	c_i
Mo potential					
10.538 63	-56.681 04	8.162 84	692.516 73	13.384 85	-124.189 11
6.949 23	619.369 04	7.319 35	-1370.460 55	11.199 18	430.778 83
5.373 66	-1540.361 98	5.125 25	2146.796 42	8.392 37	-842.869 96
4.002 99	1687.772 18	3.817 84	-2858.208 53	6.102 57	1026.555 79
2.699 29	-1202.844 95	2.707 41	2281.408 19	3.831 38	-1012.738 21
1.957 95	806.323 82	1.784 72	-1986.569 41	2.456 39	992.787 96
1.601 08	-316.694 02	1.335 72	1758.842 12	1.797 70	-616.961 47
0.316 02	-6.564 36	0.925 80	-1432.610 83	1.179 04	-32.820 92
0.213 08	9.808 06	0.780 31	873.300 98	1.161 47	193.244 94
0.182 95	-8.134 70	0.602 57	-95.557 26	0.896 98	-2.358 19
W potential					
9.035 06	13.800 84	8.565 88	-19.858 61	17.733 92	15.722 57
6.396 74	-40.673 08	6.546 96	32.976 56	12.836 48	-39.971 96
3.142 29	74.939 94	5.340 76	27.763 17	7.153 12	65.016 93
1.749 10	-41.416 21	3.298 37	-93.693 18	3.925 57	-76.877 85
1.214 89	-0.202 19	1.748 79	58.829 07	2.328 97	26.182 19
0.760 46	7.297 65	1.038 19	-30.846 09	1.420 58	-26.795 04
0.583 66	-13.073 34	0.605 12	32.764 30	0.805 60	59.122 22
0.150 97	-1.427 59	0.422 55	-5.180 86	0.596 40	-16.443 17

TABLE II. Exponential decays (α) for the Gaussian radial functions of the LCAO basis set. [See Eq. (5).]

Element	α			
Mo	4.50	1.59	0.56	0.20
W	3.00	1.22	0.49	0.20

tor in the basis space corresponding to a wave function. There is no need to fit the potential to Gaussians during the iteration procedure and the final self-consistent potential has no special shape constraint. Smith *et al.*⁸ have used a similar approach in their SCLO method for transition-metal surface calculations.

The many-electron interactions are treated with the local-density approximation using the Hedin-Lunqvist²⁷ exchange correlation for Mo and the Wigner interpolation formula²⁸ for W. For both Mo and W, there is nontrivial overlapping of the core electrons with the valence d electrons, and the nonlinearity of the exchange-correlation interaction between them is treated by the "partial core" technique.²⁹ Uniform grids of 47 k points in the irreducible portion of the Brillouin zone were used for the bcc and fcc structures and 50 k points were used for the hcp structures. Gaussian weighting in the occupancy of the electronic states near the Fermi energy was used to increase the stability of the total energy with respect to the number of k points sampled. Iterations were carried out until the Fourier components of the potentials were self-consistent to at least 0.1 mRy. By then, the total energy is stable to within 10^{-5} eV. Cohesive energies are obtained by taking the difference between the total pseudoenergy for an atom in a bulk environment and the corresponding total energy of the isolated pseudoatom in its ground state with a correction for spin-polarization energy calculated from the energy difference between spin-polarized and nonpolarized all-electron atomic calculations.³⁰

III. RESULTS

The total energy (in the pseudopotential formalism) of Mo and W at various atomic volumes close to the experimental volumes are calculated for the bcc, fcc, and hcp structures. For the hcp structure, we have assumed an ideal c/a ratio of $(\frac{8}{3})^{1/2} = 1.63$. The total (pseudo) energies are plotted against atomic volumes for Mo and W in Figs. 1 and 2, respectively. The solid lines in the figures are Murnaghan equations of state³¹ fitted to the calculated points. The equilibrium volumes, bulk moduli, and total energies at equilibrium for various structures are determined by the Murnaghan fits and are tabulated in Table III. From Figs. 1 and 2, it can be seen that the equations of state for W and Mo have many similar features:

(1) Body-centered cubic, the structure observed in nature, has the lowest energy in the calculation for all volumes calculated. The cohesive energies decrease in the order $E_{\text{coh}}^{\text{bcc}} > E_{\text{coh}}^{\text{fcc}} \approx E_{\text{coh}}^{\text{hcp}}$. At equilibrium, the fcc structures have total energies of about $\frac{1}{2}$ eV above the bcc structure (0.55 eV for W and 0.41 eV for Mo).

(2) The fcc and hcp structures are very close in energy.

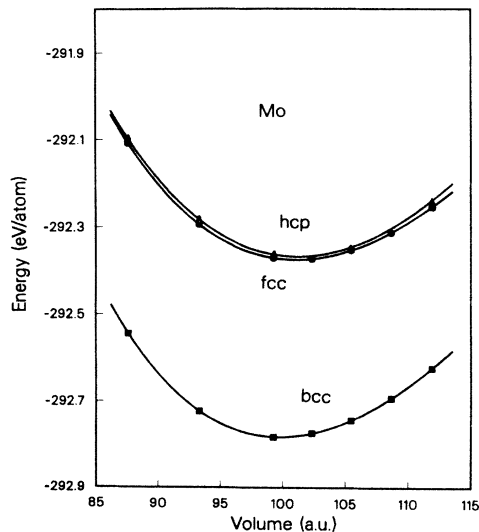


FIG. 1. Total energy (in the pseudopotential formalism) of Mo as a function of atomic volumes for bcc, fcc, and hcp (with ideal c/a ratio) structures. The solid lines are Murnaghan equations of state fitted to the calculated points.

The fcc structures are slightly more stable if the hcp structures have ideal c/a ratios of $(\frac{8}{3})^{1/2}$. The small difference in energy is not surprising as the two structures have the same first- and second-nearest neighbors. We made an estimate of the change of the total energies of the hcp structures, as the c/a ratios are changed by computing the total energies at different c/a ratios at some fixed atomic volumes. For W, the c/a ratio is changed and the

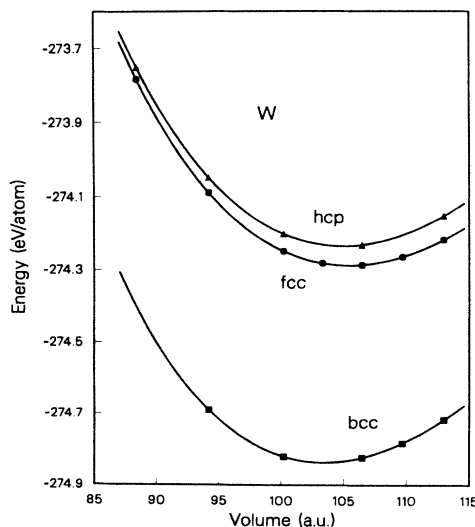


FIG. 2. Total energy (in the pseudopotential formalism) of W as a function of atomic volumes for bcc, fcc, and hcp (with ideal c/a ratio) structures. The solid lines are Murnaghan equations of state fitted to the calculated points

TABLE III. Structural properties of Mo and W in bcc, fcc, and hcp structures. The hcp structures have ideal c/a ratios of $(\frac{8}{3})^{1/2}$. The total energy (E_{total}), equilibrium atomic volume (V_0), and bulk modulus (B_0) are obtained by fitting to Murnaghan equations of state.

	Mo			W		
	bcc	fcc	hcp	bcc	fcc	hcp
E_{total} (eV)	-292.782	-292.375	-292.368	-274.837	-274.289	-274.236
$E - E_{\text{bcc}}$ (eV)	0.0	0.41	0.41	0.0	0.55	0.60
V_0 (a.u.)	99.72	101.08	101.20	103.39	105.38	104.92
B_0 (Mbar)	2.78	2.59	2.72	3.33	3.07	3.18

total energy computed at the experimental volume (which is within 1% of the equilibrium volume of the hcp structure at the ideal c/a ratio). At that volume, the total energy is found to be lowest at $c/a=1.78$ and the energy is lowered by 0.055 eV/atom. Thus, at the experimental volume, the hcp structure has virtually the same energy as the fcc structure if the c/a ratio is optimized. For Mo, we found that the changes in energy for different c/a ratios are very small near the ideal ratio. At both the experimental volume (105.463 a.u./atom) and the equilibrium volume of the hcp structure at the ideal c/a ratio (101.204 a.u./atom), the total energy changes by less than 0.01 eV/atom within 5% of the ideal c/a ratio. The structural energy difference per atom between the fcc and hcp structures for Mo at equilibrium is also only about 0.01 eV. We may conclude that near the bcc experimental volumes, the hcp and fcc structures for both elements are indeed very close in energy.

(3) The fcc structure has an equilibrium volume slightly larger than that of the bcc structure. The equilibrium volumes for the fcc and hcp (with ideal c/a ratio) structures are almost the same.

(4) The bulk modulus for W and Mo in different structures does not change very much.

The structural properties of bcc Mo and W are compared with experimental data in Table IV, and the agreement is good. Cohesive and structural properties of Mo and W in the bcc structure have been calculated accurately from first-principles within the local-density approximation (LDA) by a number of authors in recent years. Examples are Moruzzi *et al.*,⁵ Zunger and Cohen,²⁰ Fu

TABLE IV. Comparison of calculated ground-state properties of Mo and W in the bcc structure (lowest-energy structure) with experimental results. Experimental values are quoted from C. Kittel [*Introduction to Solid State Physics* (Wiley, New York, 1976)].

	Mo		W	
	Theor.	Expt.	Theor.	Expt.
Lattice constant (\AA)	3.09	3.15	3.13	3.16
Cohesive energy (eV)	7.14	6.82	9.79	8.90
Bulk modulus (Mbar)	2.78	2.73	3.33	3.23

and Ho¹⁸ for Mo, and Zunger and Cohen,²⁰ Bylander and Kleinman,^{21,22} and Jansen and Freeman²³ for W. In particular, Jansen and Freeman²³ have carefully studied W in bcc and fcc structures and found, in agreement with the present calculation, that the fcc structure has a slightly larger equilibrium volume and smaller bulk modulus. Our calculated structural energy difference of 0.55 eV is slightly larger than the 0.46 eV found by Jansen and Freeman. Our results for both Mo and W also agree well with that of Skriver³² (as estimated from Fig. 11 of Ref. 32), who calculated the structural energy differences at experimental volumes. To the best of our knowledge, the equations of state of Mo and W in the hcp structure have not been calculated from first principles before.

In Fig. 3, the Mulliken d populations³³ of Mo and W are plotted as a function of the Wigner-Seitz radius in units of the experimental radius. The hcp structures have ideal c/a ratios. The change in the Mulliken populations

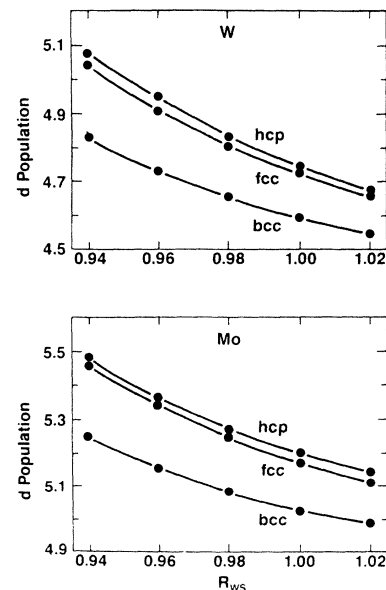


FIG. 3. Mulliken d populations for Mo and W in different structures as a function of R_{ws} , the ratio of the Wigner-Seitz radius at a particular volume to that of the experimental volume. The hcp structures have ideal c/a ratios.

for different c/a ratios of the hcp structure is found to be very small at the experimental volumes. Although the Mulliken populations do not correspond directly to experimentally measurable quantities, it is interesting to observe the trends. Similar trends are found for Mo and W. For both elements, the d population increases as the volume decreases. This is because when the volume decreases, the increase in the kinetic energy of the d electrons is slower than that of the lower-angular-momentum states, thus causing electron transfer into the d states. The change in the s populations is small (most of the s states are low in energy compared with the Fermi energy), so the increase of d populations is mainly at the expense of the p electrons. The fcc and hcp structures have very similar populations, as expected. We also see from Fig. 3 that, for the same structure, Mo has higher d populations than W.

Friedel,³⁴ Deegan,³⁵ Dalton and Deegan,³⁶ and Pettifor³⁷ have suggested that the structural trends across the transition-metal series can be explained at least semi-quantitatively by the difference in the sum of band energies. The density of states (DOS) of the bcc structure of transition metals has a well-known double-peak structure. For elements like Mo and W that have nearly half-filled bands, the Fermi energy is near the minimum between the two peaks in the DOS of the bcc structure, and thus the sum of band energies is lower in the bcc than in the fcc structure. This DOS effect accounts qualitatively for the stability of the bcc structure for elements near the middle of the transition series.³⁵ Recently, Skriver³² has calculated the crystal structure (at the experimental volumes) of nearly all $3d$, $4d$, and $5d$ elements using the difference in band energies to approximate the structural energy differences. Within the linear muffin-tin orbital (LMTO) and Anderson force-theorem³⁸ framework used by Skriver, the structural energy differences are assumed to be well approximated by differences of the sum of eigenvalues if "frozen" potentials (potentials that are not self-consistently relaxed) are used for various structures. It is interesting to see if the DOS effect is the determining factor in the relative stability of fcc and bcc structures in a self-consistent calculation. If this is the case, the difference in the sum of eigenvalues should be approximately equal to the difference in total energy for the two struc-

tures. We note that whereas the total energy does not depend on the "zero" of the crystal potential, the eigenvalues (and hence the sum of the eigenvalues) do depend on the average of the potential. Hence, we start from the same initial potential [Eq. (2)] for various structures and during the iteration to self-consistency, the $\mathbf{G}=0$ component of the potential is left unchanged. The average potentials for different structures at the same volume are thus equal. In Table V, the differences in the total energy and in the sum of eigenvalues for the fcc and bcc structures are compared. For both Mo and W, the differences in the sum of eigenvalues do have the same sign as the differences in the total energy. However, they differ in the absolute magnitude. Thus, within the present self-consistent approach, the sum of band energies correctly shows that the bcc structure is favored over the fcc structure, but it overestimates the differences in structural energies.

IV. DISCUSSION AND SUMMARY

An accurate determination of the relative stability of different phases for transition metals is challenging because the difference in structural energy is usually small (a few percent) compared with the cohesive energy, which, in turn, is small compared to the total energy. However, the determination is shown to be within reach of the local-density-functional calculations. For example, the ground-state phases are found successfully³² using the LMTO method for most of the transition elements in the Periodic Table. In the present calculations, the bcc structure is found correctly to be the ground-state phase for Mo and W. The calculated structural properties are in very good agreement with experimental data. Although the structural energy differences for W and Mo are more than an order of magnitude smaller than the corresponding cohesive energies, we still have reason to believe that they are accurate. For cohesive energies, we are comparing energies for atoms in bulk and isolated environments, and LDA's are not equally accurate in these situations. There are also convergence problems in bulk calculations, such as the completeness of the basis employed and number of \mathbf{k} points sampled. However, for similar structures in the bulk environment, like bcc, fcc, and hcp structures, these errors should cancel to a large extent and relative energies, though small, should be meaningful. Support for this assertion may be found in the fact that the structural energy differences calculated with different methods agree fairly well with each other. For example, our results agree with those obtained with the use of fully linearized augmented-plane-wave (FLAPW) calculation.²³

In summary, the present calculations, which incorporate full point-to-point self-consistency, show that the pseudopotential LCAO scheme can discriminate between energy differences among various structures for transition metals. This gives us the ability to perform structural phase studies.

Note added. Since submission of this paper, two linear augmented-plane-wave calculations of the structural properties of Mo and W have been published. Wei, Krakauer, and Weinert³⁹ treated W in bcc structure and Mattheiss

TABLE V. Comparison of the difference in total energy between the fcc and bcc structures with the corresponding difference in the sum of electronic eigenvalues. All energies are in eV. R_{WS} is the ratio of the Wigner-Seitz radius to that at the experimental volume.

R_{WS}	δE_{total}	fcc-bcc		$\delta(\sum \epsilon_i)$
		Mo	W	
1.02	0.37	0.62	0.50	0.63
1.00	0.39	0.64	0.54	0.67
0.98	0.41	0.66	0.57	0.73
0.96	0.43	0.69	0.60	0.78

and Hamann⁴⁰ calculated the structural properties of Cr, Mo, and W in both bcc and fcc structures.

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- ³⁰For both Mo and W, d^5s^1 is found to be the ground-state atomic configuration. The non-spin-polarized pseudoatoms have atomic energies of 281.29 eV for Mo and 260.87 eV for W in the d^5s^1 configuration. The spin-polarization energies (4.35 eV for Mo and 4.18 eV for W) are computed from the all-electron energy difference between the non-spin-polarized and fully-spin-polarized atoms in the d^5s^1 configuration using the Gunnarsson-Lundqvist exchange-correlation functional [O. Gunnarsson and B. I. Lundqvist, *Phys. Rev. B* **13**, 4274 (1976)].
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