

ARTICLES

Multiatom covalent bonding and the formation enthalpy of Na₂K

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We have made accurate pseudopotential calculations of the total energy of Na, K, and NaK in the CsCl structure, and Na₂K in the MgZn₂ structure. For Na₂K, the only ordered alloy known to exist, we obtained a formation enthalpy, $H = -16.1$ meV/atom, whereas for NaK we obtained $H = +7.5$ meV/atom. We argue that the negative H of Na₂K is a consequence of unusual covalent bonds involving more than two Na atoms. [S0163-1829(96)01321-5]

I. INTRODUCTION

Although sodium and potassium appear to be completely miscible and show no evidence of ordering in the liquid phase,¹⁻³ random solid alloys freeze out of the melt only in the low concentration range⁴ of less than 4.3% Na in K and, because the K atom is the larger of the two, less than 0.73% K in Na. A very careful study⁴ found that the only stable solid compound formed at atmospheric pressure is Na₂K, although there is some indication but no confirmation that NaK₂ may form at high pressure.⁵

We⁶ recently made a molecular dynamics calculation of the Gibbs free energy of liquid and crystalline Na in order to calculate its melting temperature which we obtained in fair agreement with the experimental value. We then repeated the calculation for K, obtaining somewhat better agreement with experiment. But when we attempted to calculate the freezing temperature of the liquid at the experimental eutectic concentration (32% Na), we obtained a lower free energy for the separated components than for the mixed liquid up to temperatures well above 400 K. At the experimental eutectic melting temperature⁴ of 260.5 K the phase separated liquid was 10.5 meV below the mixed. The interatomic potential as well as the large volume dependent contribution to the internal energy were obtained from linear-response theory.⁷ In order to determine whether the error in the liquid was a numerical error in the molecular dynamics or an inherent error in the linear-response theory, we calculated the 0 K formation enthalpy of Na₂K using linear-response theory, with molecular dynamics used only to find the equilibrium positions of the atoms in the unit cell. We found a positive formation enthalpy of 20.5 meV, i.e., both the 0 K compound and the liquid wanted to phase separate, contrary to experiment. Thus we concluded that the error was inherent in the linear-response theory.

The purpose of this work is first to make sure that *ab initio* calculations do result in a negative formation enthalpy for Na₂K and second to understand why it crystallizes in the complicated MgZn₂ structure when NaK does not crystallize in the CsCl structure. After all, CsCl becomes body centered cubic (bcc) when the atoms become identical and when they

are not, energy gaps open at the Brillouin zone boundary which is intersected by the Fermi surface so that one might suppose that CsCl would be a stable structure for NaK. Although it is not absolutely essential to use a local pseudopotential with linear-response theory, it simplifies the calculation greatly and is almost always done. Thus a third purpose of this work is to estimate what fraction of the error is actually inherent in linear-response theory and what fraction results from the use of a local empirical pseudopotential.

II. THE MgZn₂ STRUCTURE

Pearson's Handbook^{8(a)} lists 394 intermetallic phases which crystallize in the MgZn₂ structure, only a few of which have been sufficiently studied to have their atomic positions within the unit cell determined. To aid the reader in understanding this somewhat complicated structure, in Table I the twelve atomic positions in the unit cell are given in both hexagonal and cubic coordinates and in Fig. 1 a top and side

TABLE I. Atomic positions in the Na₂K unit cell in (a, a, c) units in both hexagonal and cubic coordinates. The subscripts on the atoms refer to the atomic positions in Fig. 1.

Atom	Hexagonal	Cubic
Na ₀	(0,0,0)	(0,0,0)
Na _{0'}	(0,0, $\frac{1}{2}$)	(0,0, $\frac{1}{2}$)
K ₁	($\frac{2}{3}, \frac{1}{3}, \bar{\zeta}$)	($\frac{1}{2}, \sqrt{3}/6, \bar{\zeta}$)
K _{1'}	($\frac{2}{3}, \frac{1}{3}, \zeta - \frac{1}{2}$)	($\frac{1}{2}, \sqrt{3}/6, \zeta - \frac{1}{2}$)
K ₂	($\frac{1}{3}, \frac{2}{3}, \zeta$)	(0, $\sqrt{3}/3, \zeta$)
K _{2'}	($\frac{1}{3}, \frac{2}{3}, \frac{1}{2} - \zeta$)	(0, $\sqrt{3}/3, \frac{1}{2} - \zeta$)
Na ₃	($\chi, 2\chi, \frac{1}{4}$)	(0, $\sqrt{3}\chi, \frac{1}{4}$)
Na ₄	($1 - 2\chi, 1 - \chi, \frac{1}{4}$)	($\frac{1}{2} - \frac{3}{2}\chi, \sqrt{3}/2 - (\sqrt{3}/2)\chi, \frac{1}{4}$)
Na ₅	($\chi, 1 - \chi, \frac{1}{4}$)	($\frac{3}{2}\chi - \frac{1}{2}, \sqrt{3}/2 - (\sqrt{3}/2)\chi, \frac{1}{4}$)
Na ₆	($1 - \chi, 1 - 2\chi, \frac{1}{4}$)	($\frac{1}{2}, \sqrt{3}/2 - \sqrt{3}\chi, \frac{1}{4}$)
Na ₇	($2\chi, \chi, \frac{1}{4}$)	($\frac{3}{2}\chi, \sqrt{3}/2\chi, \frac{1}{4}$)
Na ₈	($1 - \chi, \chi, \frac{1}{4}$)	($1 - \frac{3}{2}\chi, \sqrt{3}/2\chi, \frac{1}{4}$)

view of the hexagonal unit cell is shown with the atoms numbered as in Table I. In the following discussion we use the experimental values^{8(b)} (and calculated values in parenthesis) listed in Table II for the lattice constants a and c and the internal position parameters ζ and χ . The ratio of the Na_2K unit cell volume to 8 Na+4 K unit cell volumes is 1.020 (0.976) although if we use the room temperature values for the Na and K lattice constants the experimental ratio becomes 0.971. The values listed in Ref. 8(b) were obtained by Laves and Wallbaum⁹ who do not state at what temperature their measurements were made but it is unlikely to be below 0 °C. Thus the general principle that an intermetallic compound has a greater density than its constituents¹⁰ appears not to be violated here. Although there are open spaces in the upper left and lower right corners of the unit cell in Fig. 1, the packing of the atoms is quite efficient. The neighbors of K_2 consist of three K_1 's 8.805 (8.553) bohrs away and K_2' at 8.361 (8.603) bohrs. These can be compared with the 8.551 (8.555) bohrs nearest neighbor distance in bcc K. K_2 also has three Na_0 neighbors at 8.343 (8.182) bohrs, six Na_6 or Na_7 at 8.228 (8.181) bohrs and Na_3 , Na_4 , and Na_5 at 8.445 (8.218) bohrs. The Na forming the small triangles each actually belong to two triangles; by making two lattice translations of the figure one can easily see that Na_3 is at the center of a rectangle with Na_5 at the upper left and lower right corners and Na_4 at the other corners. These are 6.945 (6.919) bohrs away compared with the nearest neighbor distance of 6.914 (6.917) bohrs in bcc Na. The Na_3 has two second neighbors, Na_0 and Na_0' , 7.150 (7.032) bohrs away and four K_1 or K_1' , neighbors at the Na_7 - K_2 separation. The Na_0 has three each of Na_3 , Na_7 , K_2 , and K_1 neighbors at distances already given.

TABLE II. *Ab initio*, experimental, and empirical local pseudopotential equilibrium lattice constant, total energy, and bulk modulus of Na and K, lattice constant, bulk modulus, and formation enthalpy of NaK in the CsCl structure, and lattice constants, internal parameters, and formation enthalpy of Na_2K .

		<i>Ab initio</i>	Experiment	Local
Na	a (bohrs)	7.987	7.984 ^a	7.987
	E (eV)	6.273	6.251 ^{a,b}	6.259
	B (10^9 N/m ²)	7.57	7.47 ^c	7.53
K	a (bohrs)	9.879	9.874 ^a	9.874
	E (eV)	5.260	5.273 ^{a,b}	5.278
	B (10^9 N/m ²)	3.87	3.66 ^d	3.74
NaK	a (bohrs)	8.983		
	B (10^9 N/m ²)	5.14		
	H (meV/atom)	7.5	Positive	
Na_2K	a (bohrs)	13.959	14.173 ^e	14.075
	c (bohrs)	22.966	23.225 ^e	23.035
	χ	0.1680	0.170 ^e	0.1678
	ζ	0.0627	0.070 ^e	0.0627
	H (meV/atom)	-16.1	Negative	2.8 meV

^aReference 16.

^bReference 15.

^cReference 17.

^dReference 18.

^eReference 8(b).

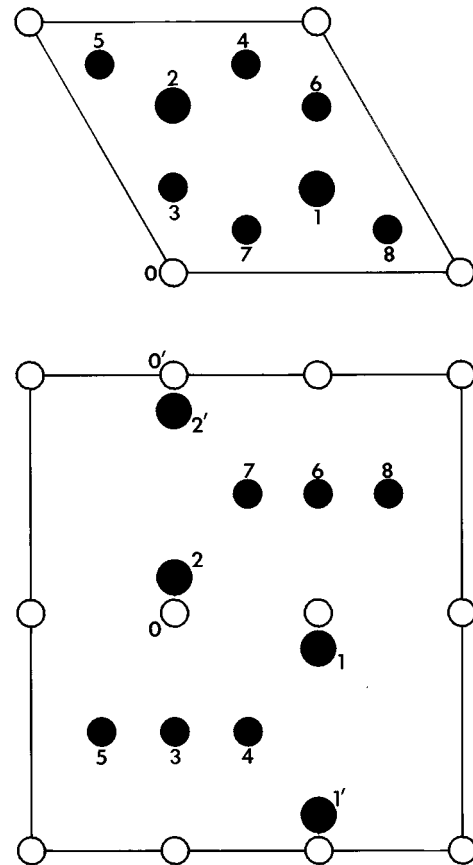


FIG. 1. Top and side views of the hexagonal Na_8K_4 unit cell. The black and white small circles are Na atoms and the large black circles are K's. The atoms are numbered according to Table I.

III. CALCULATIONS AND RESULTS

We performed Dirac Hartree-Fock (HF) calculations for Na and K. Then freezing the core, occupied p and d eigenfunctions were calculated (the latter for K only). The large component of the Dirac wave functions were extended smoothly¹¹ from $r_{\text{Na}}=2.4$ bohrs and $r_{\text{K}}=3.2$ bohrs in a norm conserving fashion back into the nucleus and inserted into the Schrodinger equation which was inverted to obtain the atomic pseudopotentials. The ionic pseudopotentials are identical to the atomic in this monovalent case because HF electrons do not see themselves. The spin-orbit interaction which gives a negligible contribution to the energy of the solid is eliminated by taking the $2j+1$ weighted average of the $j=l\pm\frac{1}{2}$ pseudopotentials. The Na HF pseudopotential, when used in the crystal with a local density approximation (LDA) valence electron exchange-correlation potential, results in an equilibrium lattice constant of 8.159 bohrs and a total energy of 6.159 eV; these represent 2.2% and 1.5% discrepancies with the experimental values listed in Table II. Because they are so soft, the errors in the calculated lattice constants of Na and K tend to be quite large. The discrepancy here is actually quite a bit smaller than that which resulted with our original HF core pseudopotential¹² which differs from this one in two ways.¹³ However, because the positive and negative formation enthalpies of NaK and Na_2K are so small, we felt it important to construct pseudopotentials which yield better results for Na and K. Our philosophy is if first principles cohesive energy calculations are per-

formed with pseudopotentials chosen to fit atomic eigenvalues (although only in one case of which we are aware is the total atomic valence energy for a multivalent atom¹⁴ also fit), then averages of two such first principles pseudopotentials which fit properties of the constituent metals may be used to calculate the formation enthalpy of the intermetallic compound. We therefore calculated pseudopotentials for LDA ions and with a 96.5% (93.2%) HF and 3.5% (6.8%) LDA pseudopotential average for Na(K) obtained the equilibrium lattice constants, total energies, and bulk moduli compared in Table II with low temperature experimental values where E is the sum of the ionization¹⁵ and cohesive¹⁶ energies and B is obtained from published elastic constants.^{17,18} (The pseudopotential was factorized¹⁹ after it was averaged.)

The calculations were well converged, using all plane waves with $(\mathbf{k}+\mathbf{K})^2 < 20$ Ry and sampling 112 \mathbf{k} points in the (1/48)th irreducible wedge of the Na and K Brillouin zones, 56 \mathbf{k} points in the NaK (1/48)th irreducible wedge, and 48 \mathbf{k} points in the Na₂K (1/24)th irreducible wedge. On going from a 40 \mathbf{k} -point to the 112 \mathbf{k} -point sample the Na total energy changed by 4.6 meV.

It is interesting to note that the calculated lattice constant and total energy of NaK in the CsCl structure are close to the average of the Na and K values but slightly closer to K, resulting in a positive (i.e., endothermic) formation enthalpy. The NaK bulk modulus is far from the average of the Na and K values but its inverse, the compressibility, is, to within the accuracy of its calculation, equal to the average of the Na and K compressibilities.

As mentioned previously, much of the difference between the calculated and experimental lattice constants and internal cell parameters arises from the temperature at which they were measured.⁹ The rest can be attributed to the poor quality of the samples and errors inherent in LDA calculations. Not only is the calculated compound to constituent volume ratio less than unity whereas the measured is not but also the calculated K-K bond lengths are more nearly equal, as are the K-Na bond lengths, than the measured values. Each K sits in a tetrahedron of K's where the ratio of the distance of the atom from its neighbor along the z axis to its distance from its three other neighbors is calculated to be 1.006 whereas experimentally it is 0.9496. Similarly each K has six black (in Fig. 1) Na atom neighbors and three white with a calculated black to white distance ratio of 0.9999 whereas experimentally the ratio is 0.9862. Most importantly, however, Na₂K has a calculated formation enthalpy of -16.1 meV/atom.

We may now ask why NaK has a positive formation enthalpy while that of Na₂K is negative, noting that the sign of the change in volume on forming the compound is the same as that of the formation enthalpy in both cases. Both Na and K may be considered to be point ions with repulsive cores floating in a free electron gas which responds fairly weakly to the sum of the repulsive core and attractive ionic potentials. The hard cores of the atoms do not overlap so the equilibrium electron density is determined by the minimization of the jellium kinetic, exchange and correlation energy, the Madelung energy of point ions in a constant compensating charge density and the energy of the electron gas in the repulsive core potential. Only the last of these is species dependent. In addition there is a contribution from the re-

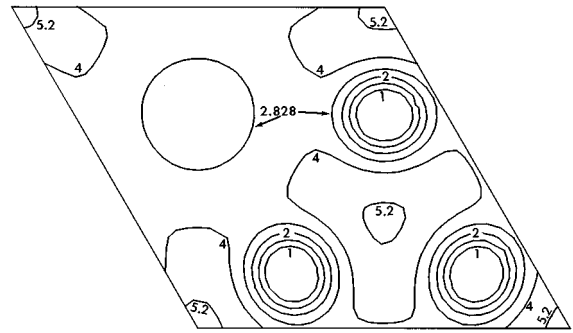


FIG. 2. Contours of constant pseudocharge density in the plane containing Na atoms labeled 6, 7, and 8 in Fig. 1. The units are millielectrons/bohr³. Except for the 5.2 contour, the contours increment by a factor of $\sqrt{2}$.

sponse of the electron gas to the repulsive core and attractive ionic potentials. Thus because of their different core sizes, Na and K minimize their total energy with different lattice constants, and we show in the Appendix that if one neglects the response of the electron gas so that the energy depends only on the volume, the average energy of the phase separated system will be lower than the energy of the alloy for any free electron system. The response of the electron gas lowers the energy of the alloy relative to its constituents because it opens up energy gaps near the Fermi surface. For Na₂K the response energy gain of the alloy over its constituents overcomes the volume dependent energy reduction whereas for NaK it does not.

That Na₂K has a larger electron response than one would expect for an alkali metal alloy can be seen in Fig. 2 where contours of constant pseudocharge density are plotted in the plane containing the Na₆, Na₇, and Na₈ atoms. The pseudocharge density is the charge density of the pseudoconduction electron wave functions. Since only the conduction electrons contribute to the binding, this is the appropriate charge density to plot. The pseudofunctions are identical to the true wave functions outside the atomic cores and inside contain the same total charge but with its density redistributed. Because of the nodes in the conduction wave functions, inside the cores the pseudocharge density is quite small. We see a strong Δ bond²⁰ represented by the peak of 5.2 millielectrons per cubic bohr (me/a_0^3) at the centroid of the Na triangle. This can be compared with the maximum charge density in Na, which has an average charge calculated to be 26.6% larger than Na₂K. Its maximum was found to be only 4.43 me/a_0^3 . Figure 3 is a contour plot in the plane containing the long diagonal of Fig. 2 and the z axis. Note that there are two different kinds of Na triangles. The one seen explicitly in Fig. 2 has K atoms $c(\frac{1}{4} + \zeta)$ above and below its centroid and the one formed by Na₈ and lattice vector translations of Na₇ and Na₆ which has “white” Na atoms $\frac{1}{4}c$ above and below its centroid. Both 5.2 me/a_0^3 contours have similar cross sectional areas in the plane of the triangles but the one with Na caps is more than four times longer along the z axis. This might better be called a stretched tetrahemihexahedral bond. We are aware of no other case in which electronic charge appears to be trapped inside a cluster of atoms. See Ref. 21(b) for an example in which the charge becomes vanishingly small at the center of a cluster.

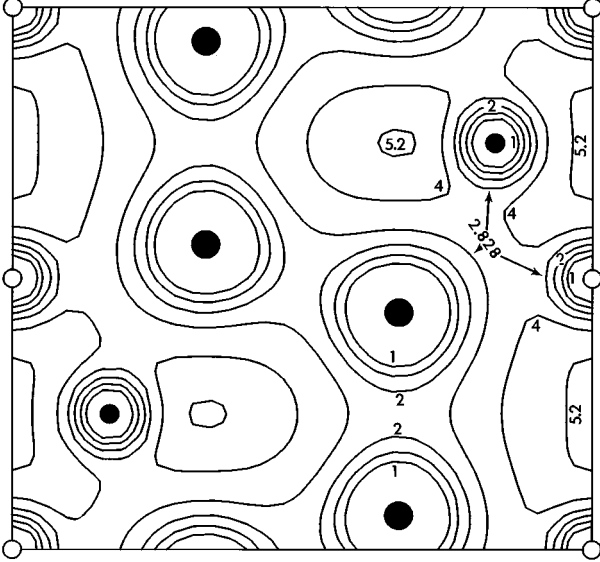


FIG. 3. Contours of constant pseudocharge density (plotted as in Fig. 2) in the plane containing the long diagonal of Fig. 2 and the z axis.

In order to determine whether the failure⁶ of linear-response theory to yield a negative formation enthalpy for Na_2K was a consequence of using a local pseudopotential or an inherent failure of linear-response theory, we have constructed local empirical pseudopotentials which yield equal or better agreement with the experimental Na and K lattice constants, total energies, and bulk moduli than the first principles pseudopotentials did. Except for the difference in pseudopotentials, the calculations whose results are displayed in the ‘‘*Ab initio*’’ and ‘‘Local’’ columns of Table II are identical. The local ionic pseudopotentials were taken to have the form

$$V = \alpha V_s + \beta V_p + \frac{2}{r} (\alpha + \beta - 1),$$

where V_s and V_p are the unfactorized s and p pseudopotentials used in the first principles calculations and the last term insures that for large r the ionic pseudopotential goes to $-2/r$. For Na, $\alpha = \beta = 0.5325$ whereas for K, $\alpha = 0.60363$ and $\beta = 0.22667$. Our first principles K calculation required a d pseudopotential which may account for the large difference between the values of the Na and K parameters required to fit the experimental values. Note that for Na the potential goes to $0.13/r$ Ry for $r \rightarrow 0$ whereas for K it goes to $-0.3394/r$ Ry. This sign difference was also found in the local pseudopotentials constructed for the linear-response calculations.⁶ Although the local pseudopotential Na_2K lattice constants are in better agreement with experiment than the first principles calculations, this probably does not represent an improved result, rather it is consistent with the rule that the less the binding the greater the volume and the fact that the experimental results were not obtained near 0 K. What is significant is that the calculated formation enthalpy is 2.8 meV, almost exactly midway between the linear response value of 20.5 meV and the first principles -16.1 meV. Thus it ap-

TABLE III. Equilibrium value of r_s in Eq. (1) for three different values of the parameter A and the energy obtained therefrom.

A	$r_s^{(0)}$	E (eV)
10	4.10	-6.2001
12	4.395	-5.8451
16	4.92	-5.3053

pears that the error introduced by using linear-response theory is about half inherent and half a consequence of using a local pseudopotential.

We have also examined charge density contour plots for the local pseudopotential full-quantum-mechanical and linear-response-theory calculations. (The charge density does not explicitly enter the latter calculation but it is easily obtained from the pseudopotential and the dielectric function.) In the quantum mechanical case the $5.2 \text{ me}/a_0^3$ contour inside the tetrahemihexahedron is reduced in size and disappears completely from the Δ bond where the maximum density is $5.1 \text{ me}/a_0^3$. Although we had no *a priori* reason to expect that the local pseudopotential would result in less total energy and weaker bonds than the nonlocal, the weaker bonds are consistent with the reduced energy. In the linear response case the $5.2 \text{ me}/a_0^3$ contours were essentially replaced by $4.3 \text{ me}/a_0^3$ contours. This large reduction in covalent bonding we had expected based on our knowledge of the diamond covalent bond.²² The $(2,2,2)$ Fourier component of the unscreened crystal pseudopotential vanishes because of a structure factor in diamond. Therefore $\rho(2,2,2)$ vanishes in linear-response theory. However, both the experimental and calculated $\rho(2,2,2)$ are of the same magnitude as the other Fourier components, with the exception of $\rho(1,1,1)$. The sign of the experimental $\rho(2,2,2)$ is not determined but the calculated $\rho(2,2,2)$ had its maximum at the center of the covalent bond and without it the bond would have been much weaker. Thus it is $V(1,1,1)$ acting two or more times in higher order perturbation theory that gave the large bond. Similarly in Na_2K the bonds are made much stronger by the higher order response of the electron gas.

In conclusion, our calculations have found, in agreement with experiment, that Na_2K has a negative formation enthalpy while that of NaK in the CsCl structure is positive. In addition we have shown that if the electron gas is not allowed to respond, the alloy always has a positive formation enthalpy and it is the formation of strong Δ and stretched tetrahemihexahedral bonds that results in the negative formation enthalpy of Na_2K .

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APPENDIX

We here show that the alloying of two nearly free electron metals causes a reduction in the energy coming from those contributions which depend only on the density of the nonresponding electron gas. We have

$$E = \frac{2.21}{r_s^2} - \frac{2.716}{r_s} + \frac{A}{r_s^3} - 0.045 \left\{ \left[1 + \left(\frac{r_s}{21} \right)^3 \right] \ln \left(1 + \frac{21}{r_s} \right) + \frac{r_s}{42} - \left(\frac{r_s}{21} \right)^2 - \frac{1}{3} \right\}, \quad (\text{A1})$$

where the first term is the kinetic energy of the free electron gas and the second term combines the exchange energy $-0.916/r_s$ of the electron gas with the Coulomb energy of any reasonable arrangement of point charges in a compensating constant background of charge density, which is approximately $-1.8/r_s$. The fourth term is the correlation

energy.²³ The third term represents $\int \hat{V}(r)\rho d^3r$ where $\hat{V}(r)$ is the repulsive short range part of the ionic pseudopotential [i.e. $\hat{V}(r) = V(r) + 2/r$ where $V(r)$ is the ionic pseudopotential] and ρ is the constant electronic charge density. $A = 10$ corresponds closely to Na and $A = 16$ to K as can be seen from the equilibrium lattice constants $r_s^{(0)}$ and energies listed in Table III. $A = 12$ then represents the appropriate average $\int [\frac{2}{3}\hat{V}_{\text{Na}}(r) + \frac{1}{3}\hat{V}_{\text{K}}(r)]\rho d^3r$ for Na_2K . We see that $E(\text{Na}_2\text{K})$ lies 56.7 meV above $\frac{2}{3}E(\text{Na}) + \frac{1}{3}E(\text{K})$ and therefore were it not for the large energy band contribution to the energy (relative to Na and K), Na_2K would have a positive formation enthalpy.

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¹³The pseudopotential of Ref. 12 approached the true potential with

increasing r , the difference being reduced to 1% at $1.5r_c = 2.55$ bohrs, whereas in the current case the difference completely vanishes at $r_{\text{Na}} = 2.4$ bohrs. The previous pseudopotential was obtained from an atom in which all the electrons saw a HF potential from the core electrons and a LDA potential from the valence electrons whereas the present atomic calculation is strictly HF.

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