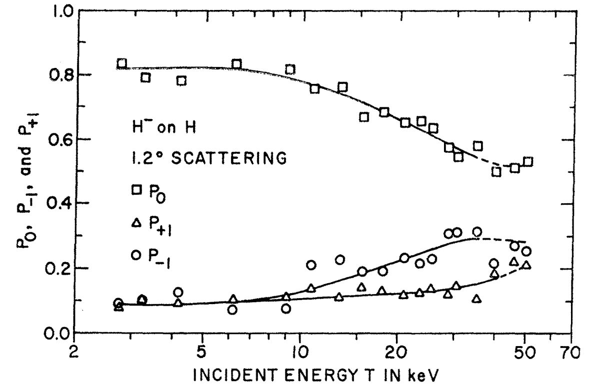

FIG. 3. These data concern the H⁻-on-H collision wherein the incident particle is scattered at 1.2°. The charge-state probabilities P_0, P_{+1}, and P_{-1} are plotted versus the incident H⁻ ion's energy.

are not well established by the data. The oscillations in reaction D are apparently a new phenomenon.

H on H_2

Figure 2 shows the 3° scattering data for this combination. There is a peak to the H⁻ production at 12 keV and a corresponding dip in the H⁺ production at the same energy. The neutral component, not shown since $P_0 = 1 - P_{+1} - P_{-1}$, remains fairly constant at about 75% over the energies studied here.

H⁻ on H

Figure 3 shows the H⁻-on-H data for scattering of the fast particle at 1.2°. The charge-state fractions P_0, P_{+1}, and P_{-1} change slowly with energy. Lichten[7] has suggested that there may be oscillations in the resonant reaction $H^- + H \rightarrow H + H^-$. If present, these should show in the P_{-1} component in Fig. 3. The evidence here is that any such oscillations are of sufficiently small amplitude to be entirely masked by the scatter of the data.

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Theoretical Electron Affinities for Some of the Alkali and Alkaline-Earth Elements*

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The $(ns)^2$ correlation energies for the negative ions Li⁻, Na⁻, and K⁻ have been calculated by the method of superposition of configurations. Comparisons with Hartree-Fock calculations of the neutral species yield electron affinities of 0.62, 0.54, and 0.47 eV, respectively. A study of the computed ionization potentials of the neighboring isoelectronic atoms and ions suggests a maximum uncertainty of 0.1 eV. Similar calculations of the $ns(np)^2\,{}^4P$ states of Be⁻ and Mg⁻ indicate that they are metastable, with electron affinities, relative to the $nsnp\,{}^3P$ state of the neutral atom, of 0.24 and 0.32 eV, respectively.

INTRODUCTION

A RECENT determination of the electron affinity of the lithium atom[1] is quite remarkable in that it is the *only* experimental determination, to date, of the electron affinity of any of the alkali metals. While there have been numerous calculations and isoelectronic sequence extrapolations, which appear to provide some sort of consensus for Li⁻, this is not the case for Na⁻, where values are found to be scattered from 0.14 to 0.78 eV. The data available for the heavier alkalis is much more sparse.[2,3] Also, mass-spectrometer observations of Be⁻ and Mg⁻ have recently been reported,[4] although no electron affinity has been given. It is not clear here what state of the negative ion may be involved.

This paper reports the results of variational superposition of configurations calculations on these ions and atoms, which are designed to account for just enough of the correlation energy to yield significant predictions of the electron affinities. The calculations are based on three assumptions concerning the behavior of the correlation energy. To begin with, it is supposed that the total energy of the ion (or atom) is well represented by the "pair-correlation energy" formula[5]

$$E = E_0 + \sum_{ij} \epsilon_{ij}\,, \tag{1}$$

where E_0 is the Hartree-Fock (HF) total energy and ϵ_{ij} is the correlation correction associated with the ij electron pair. It is generally believed that pair interactions make the dominant contribution to the correla-

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[1] B. Ya'akobi, Phys. Letters **23**, 655 (1966).

[2] L. M. Branscomb, *Atomic and Molecular Processes* (Academic Press Inc., New York, 1962), p. 100.

[3] B. L. Moiseiwitch, *Advances in Atomic and Molecular Physics* (Academic Press Inc., New York, 1965), Vol. 1, p. 61.

[4] K. Bethge, E. Heinicke, and H. Baumann, Phys. Letters **23**, 542 (1966).

[5] O. Sinanoğlu, J. Chem. Phys. **36**, 706 (1962).

tion energy, and this has been supported by various calculations, such as, for example, some recent work on the oxygen atom.[6] Secondly, it is assumed that the correlation energy of the core electrons does not change significantly when one of the outer electrons is removed. The core electrons occupy a physically different region of space than do the valence electrons and so should be expected to be only slightly affected by outer-shell excitations, much of which would already be taken into account by the relaxation of the Hartree-Fock core. The final assumption is that the intershell-correlation energy, which is small to begin with for electrons in different quantum shells, will change by only a small amount when one of the outer electrons is removed. The last two assumptions are supported by calculations of excitation and ionization energies for magnesiumlike[7,8] and sodiumlike[9] atoms and ions.

Thus, for an alkalilike atom, with N electrons, and the $(N+1)$-electron system formed by binding one more electron into an $(ns)^2$ configuration, the total energies are

$$E(N)=E_0(N)+\epsilon(ns-\text{core})+\epsilon(\text{core})\,, \tag{2a}$$

$$E(N+1)=E_0(N+1)+\epsilon(ns^2)+\epsilon(ns^2-\text{core})+\epsilon(\text{core})\,, \tag{2b}$$

where the ϵ summations of (1) have been grouped according to the type of correlation involved. Given the above assumptions, the problem of calculating an ionization, or detachment, energy then comes down to calculating the $(ns)^2$ correlation energy, and this has been done here by the method of superposition of configurations (SOC). It should be noted that the assumptions just made are somewhat stronger than implied by Eq. (1), since ϵ(core) can also include higher-order (three- and four-body) correlation corrections.

The SOC approximation consists of writing a trial function as a linear superposition of terms,

$$\psi=c_0\Phi_0+\sum_{a,i} c_a{}^i\Phi_a{}^i+\sum_{a,i}\sum_{b,j} c_{ab}{}^{ij}\Phi_{ab}{}^{ij}\,, \tag{3}$$

where Φ_0 is the Hartree-Fock function, and the notation means replace the occupied orbital a by some virtual "excited" orbital i, etc. Application of the variational principle to this function leads, in the usual way, to a secular equation for the coefficients and total energy. To compute the $(ns)^2$ correlation energy of an alkali negative ion, only those terms are added to the Hartree-Fock function in (3) which correspond to virtual-orbital substitutions of the outer two valence electrons.

TABLE I. Breakdown of the computed total energies (in a.u.) for Na$^-$, $3s^2\ {}^1S$.

No. of configurations	Configurations	$-E_{\text{tot}}$	ΔE
1	$3s^2$	161.8548	0.0
2	$3s^2+3p^2$	161.8749	0.0201
3	$3s^2+3p^2+3d^2$	161.8751	0.0203
8	3-config.$+3s4s+4s^2+4p^2+4d^2+4f^2$	161.8784	0.0236
10	8-config.$+3s5s+5s^2$	161.8787	0.0239

The analytical expansion method Hartree-Fock procedure[10] has been used to obtain the relevant Hartree-Fock functions, and a pseudonatural orbital transformation, described in some detail elsewhere,[11] was used to generate the SOC virtual orbitals. In the case of the alkali negative ions, this amounts to simply obtaining the natural orbitals for the ns^2 two-electron system.[12] From the Hartree-Fock basis of Slater-type functions, augmented by the addition of basis functions of different symmetry, a set of virtual orbitals is generated by an arbitrary Schmidt orthogonalization. These orbitals are then used in a complete SOC calculation, i.e., all possible combinations of them are used in (3) for the valence-pair substitutions. The energy for this function is minimized with respect to the parameters of the additional basis functions and then a natural orbital transformation carried out to determine an "optimum" set of orbitals. While this introduces nothing new for two-electron systems, it produces a much more compact SOC wave function, and the occupation numbers provide a natural way of ordering the virtual orbitals according to their importance in the wave function. For an atom with more than two electrons, this procedure is applied to a single pair, and the pseudonatural orbitals (PSNO) so obtained are then used to correlate all the other strongly interpenetrating electron pairs. In the present calculations, the Hartree-Fock occupied orbitals are retained instead of the first natural orbitals.

ALKALI ELECTRON AFFINITIES

Table I gives the energy results, in a.u.,[13] obtained for Na$^-$, as an example of the kind of calculation that has been done in general. In every case a sequence of SOC wave functions has been computed, successively using more terms containing the higher-order PSNO's. As a still more detailed example, the final 10-configuration Na$^-$ wave function is given in an Appendix. It should be noted that single-excitation configurations,

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[6] H. P. Kelly, Phys. Rev. **144**, 39 (1966).

[7] R. N. Zare, J. Chem. Phys. **45**, 1966 (1966).

[8] A. W. Weiss, J. Chem. Phys. **47**, 3573 (1967).

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[12] P. O. Löwdin and H. Shull, Phys. Rev. **101**, 1730 (1956).

[13] Atomic units, unless otherwise noted, are used throughout this paper. The energy unit (in a.u.) = 27.21 eV.

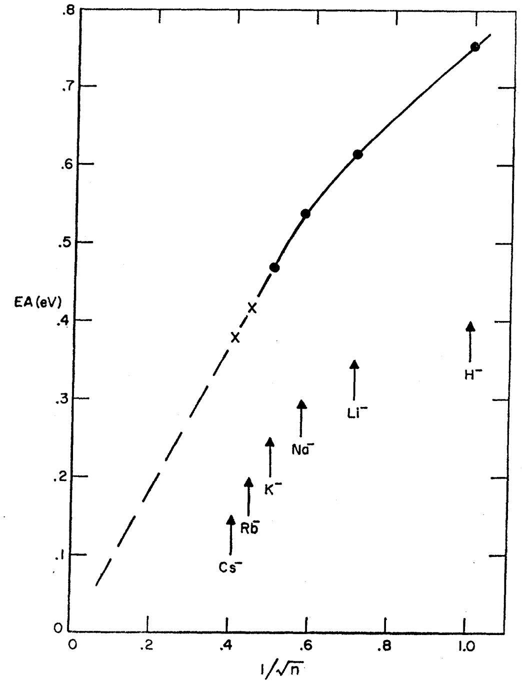

FIG. 1. The alkali-metal electron affinities versus $n^{-1/2}$, where n is the principal quantum number.

TABLE II. Total energies, electron affinities, and ionization potentials (in a.u.) for the alkalis (Li, Na, and K) and some of their isoelectronic ions.

	Total energy		Ionization potential		
	$(ns)^2\,{}^1S$ (SOC)	$ns\,{}^2S$ (HF)[a]	Calc.	Expt.[b]	Error
		$n=2$			
Li^-	−7.4553	−7.4327	0.0226	0.022	0.001
Be	−14.6189	−14.2774	0.3415	0.3426	0.0011
B^+	−24.2985	−23.3760	0.9225	0.9241	0.0016
C^{+2}	−36.4832	−34.7261	1.7571	1.7598	0.0027
		$n=3$			
Na^-	−161.8787	−161.8589	0.0198	...	...
Mg	−199.6480	−199.3715	0.2765	0.2810	0.0045
Al^+	−241.7143	−241.0304	0.6839	0.6919	0.0080
Si^{+2}	−288.0409	−286.8211	1.2198	1.2309	0.0111
		$n=4$			
K^-	−599.1818	−599.1646	0.0172	...	...
Ca	−676.7863	−676.5698	0.2165	0.2247	0.0082
Sc^+	−759.4962	−758.9805	0.5157	0.5333	0.0176
Ti^{+2}	−847.2694	−846.3802	0.8892	0.9088	0.0196

[a] See Ref. 14. [b] See Refs. 15, 16.

such as $3s4s$, are of some importance, since the Hartree-Fock $3s$ function is used instead of the first natural orbital. While the number of configurations needed varied somewhat from atom to atom, approximately 10 configurations were normal for the members of the Be, Mg, and Ca sequences. The results of Table I strongly suggest that most of the $(3s)^2$ correlation energy has been recovered by this calculation, and this is generally the case for all the $(ns)^2$ systems treated here.

The final energy results are given in Table II for Li^-, Na^-, and K^-, and, in each case, for the three neighboring isoelectronic systems.[14] The ionization potentials and electron affinities have been computed as the difference between the SOC total energy for $(ns)^2$ and the Hartree-Fock energy of the ns atom, with one less electron. The experimental data is taken from Atomic Energy Levels,[15] with the exception of Ti^{+2}, where more recent data have been used.[16] Probably the most significant observation concerns the errors and error trends in the computed ionization potentials. In every case, the error decreases toward the neutral end of the sequence and should probably be still substantially smaller for the negative ion. This effect is not at all surprising and can easily be understood as a decrease in the correlation energy as the wave function becomes more diffuse. A rough graphical extrapolation of the errors leads to a predicted error of 0.02 eV for Li^- and 0.01 eV for Na^-. The error plot for the Ca sequence does not yield anything, and it appears that the Sc^+ data may be in error. At any rate, the directly computed affinities, in eV, are 0.62, 0.54, and 0.47 for Li, Na, and K, respectively, and the error trends suggest that it is not unreasonable to assign a maximum uncertainty of 0.1 eV.

The results of a number of extrapolations[17–19] and other calculations[20–23] have been collected in Table III for comparison with these predictions. For lithium, the consensus seems to indicate an electron affinity of

TABLE III. A comparison of extrapolated and calculated electron affinities (in eV) for the alkalis.

	Extrapolations				Calculations		
	K[a]	C[b]	E[c]	HF[d]	Pseudo-potential[e]	This work[f]	Expt.[g]
Li	0.64	0.59	0.82	0.58	0.43	0.62	0.6
Na	0.14	0.22	0.47	0.78	0.53	0.54	
K				0.90	0.49	0.47	
Rb					0.43	(0.42	
Cs					0.42	(0.39)	

[a] M. Kaufman, Ref. 17.
[b] R. J. S. Crossley, Ref. 18.
[c] B. Edlén, Ref. 19.
[d] Hartree-Fock plus correlation energy estimate (Clementi *et al.*, Refs. 20–22).
[e] L. Szász, Ref. 23.
[f] The Rb and Cs values have been estimated graphically; see text.
[g] B. Ya'akobi, Ref. 1.

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[14] For the Hartree-Fock values, see E. Clementi, J. Chem. Phys. 38, 996 (1962); 38, 1001 (1962); 41, 295 (1964).

[15] C. E. Moore, *Atomic Energy Levels* (National Bureau of Standards Circ. No. 467, U. S. Government Printing Office, Washington, D. C., 1949), Vol. 1; *Selected Tables of Atomic Spectra*, NSRDS-NBS 3 (U. S. Government Printing Office, Washington, D. C., 1965).

[16] B. Edlén (private communication).

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[19] B. Edlén, J. Chem. Phys. **33**, 98 (1960).

[20] E. Clementi and A. D. McLean, Phys. Rev. **133**, A419 (1964).

[21] E. Clementi, A. D. McLean, D. L. Raimondi, and M. Yoshimine, Phys. Rev. **133**, A1274 (1964).

[22] E. Clementi, Phys. Rev. **135**, A980 (1964).

[23] L. Szász, Acta Phys. Hung. **6**, 307 (1956).

TABLE IV. Breakdown of the computed total energies (in a.u.) for Be^-, $2s2p^2\,{}^4P$.

No. of configurations	Configurations	$-E_{tot}$	ΔE
1	$2s2p^2$	14.50901	0.0
8	$2s(2p^2+3p^2+3d^2)+(3s+3d)2p^2$ $+(2s3p+3s3p+3p3d)^3P2p$	14.52641	0.01740
18	8-config.$+2s(4p^2+3p4p+4d^2+3d4d)$ $+(2s4p+3s4p+4s4p+4p3d+3p4d+4p4d)^3P2p$	14.52721	0.01820
20	18-config.$+(2s5p+5p4d)^3P2p$	14.52736	0.01835

approximately 0.6 eV, in agreement with the experimental determination and disagreeing somewhat with the otherwise quite successful extrapolations of Edlén. This also agrees with the value of 0.62 eV obtained earlier from a complete atom SOC calculation combined with error estimates.[24] Except for lithium, the present results agree quite well with the pseudopotential calculations of Szász.[23] Szász made a strictly two-electron, variational calculation, with an effective potential inserted into the Hamiltonian to represent the effect of the core, which is thus very much in the spirit of the work reported here. He used the Hellmann potential, with the parameters adjusted to give a best fit to the lower energy levels of the neutral alkali. The exception to this was lithium, where a somewhat different procedure was used to determine the potential, and this appears to account for the Li^- discrepancy.

The affinities calculated here decrease with increasing principal quantum number, n. This behavior is shown in Fig. 1, which also includes the well-known H^- value.[25] For what it may be worth, values for Rb and Cs have been extrapolated from the graph, and they are also included in Table III. If one includes these extrapolations, then, except for lithium, the results of this paper are in remarkably good agreement with those of Szász. This decrease in electron affinity for the heavier alkalis is exactly opposite to the trend indicated by the Hartree-Fock calculations with correlation energy estimates,[20–22] suggesting that the correlation estimates may be somewhat in error for Na^- and K^-.

ALKALINE-EARTH ELECTRON AFFINITIES

Since the alkaline-earth ground-state configurations are $(ns)^2\,{}^1S$, i.e., already closed shells, there is some question as to the state of the negative ion as well as the value of the affinity. Since it appears to be generally agreed that the normal ground state $(ns)^2np$ is unstable,[2,3] there has been some conjecture that the lowest-lying Rydberg state is stable.[3,4] For example, Be^- would then be formed as

$$\mathrm{Be}(2s)^2\,{}^1S \rightarrow \mathrm{Be}^-(2s)^2 3s\,{}^2S. \tag{4}$$

Attempts were made to compute this state in both the Hartree-Fock and SOC approximations, in the latter case allowing for correlation in the $(2s)^2$ of the neutral atom and the $(2s)^2 3s$ of the negative ion. In both cases, it was found that, in attempting to minimize the energy, the energy of the negative ion remained above that of the neutral, moving down towards it as the $3s$ became more and more diffuse. It seems clear that the variational principle is trying to make the $3s$ orbital look like a free-electron function—a well-known phenomenon for unstable states.[20,24]

Failing this, attention was turned to determining a metastable negative-ion state. The most likely candidate for Be^- is then the $2s(2p)^2\,{}^4P$, which would have

TABLE V. Energies (in a.u.) for Hartree-Fock and superposition of configurations (SOC) calculations on Be^-, Mg^-, and some isoelectronic atoms and ions.

	Hartree-Fock Total energy			SOC Total energy			Experimental[a]	Error	
	$ns(np)^2\,{}^4P$	$nsnp\,{}^3P$	Ionization potential	$ns(np)^2\,{}^4P$	$nsnp\,{}^3P$	Ionization potential	Ionization potential	H-F	SOC
				$n=2$					
Be^-	−14.5090	−14.5115	0.0025	−14.5274	−14.5184	−0.0089	···		
B	−24.4507	−24.1202	−0.3305	−24.4682	−24.1275	−0.3407	−0.3439	0.0134	0.0032
C^+	−37.1610	−36.2357	−0.9252	−37.1784	−36.2433	−0.9351	−0.9388	0.0136	0.0037
				$n=3$					
Mg^-	−199.5506	−199.5466	−0.0040	−199.5649	−199.5530	−0.0119	···		
Al	−241.7908	−241.5427	−0.2481	−241.8058	−241.5497	−0.2561	−0.2583	0.0102	0.0022
Si^+	−288.4331	−287.7993	−0.6338	−288.4495	−287.8069	−0.6426	−0.6459	0.0121	0.0033

[a] See Ref. 15.

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[24] A. W. Weiss, Phys. Rev. **122**, 1826 (1961).
[25] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).

to lie below the $2s2p\ ^3P$ first excited state of Be, autoionization to the ground state being spin-forbidden. Here, the original SOC calculations for determining the pseudonatural orbitals were made on the $2s$-$2p$ pair. These PSNO's were then used as the virtual orbitals of a full SOC calculation, including, for example, excitations of the $(2p)^2$ pair. The final energy results for Be^- are given in Table IV. The convergence of the energies suggests that most of the three-electron, $2s(2p)^2$, correlation energy has indeed been recovered. Since all three electron spins are parallel, the correlation problem here should not be very severe anyway.

All the final results for Be^-, Mg^-, and some neighboring isoelectronic atoms and ions are collected in Table V. Similar SOC calculations were also made on the $nsnp\ ^3P$ states, in order to have the appropriate reference for the ionization-potential (or electron-affinity) calculation. The magnesium-sequence triplet results have been published previously.[8] It can be seen that ionization potentials for the neutral atom and positive ions are fairly accurate, the maximum error being (for C^+) approximately 0.1 eV, and it seems unlikely that the affinities are any less accurate. The computed metastable electron affinities are 0.24 and 0.32 eV for Be and Mg, respectively. It should also be noted that the correlation corrections, although small, are important, since Be^- is not even metastable in the Hartree-Fock approximation, and the value for Mg^- differs substantially from the SOC calculation.

Since it appears that these ions are metastable, the next question, and one which unfortunately is outside the scope of this paper, is what are their lifetimes against auto-ionization due to weak interactions, such as direct spin-spin or indirect spin-orbit coupling to the continuum. If, as seems reasonable, the lifetimes are in the microsecond range, then the negative ions observed in the mass spectrometer could well be these metastable species. However, more definite conclusions will have to await calculations or measurements of the lifetimes.

ACKNOWLEDGMENTS

All the Hartree-Fock calculations made here were carried out with an IBM 7094 computer program written by the personnel of the Laboratory of Molecular Structure, University of Chicago, under the supervision of Professor C. C. J. Roothaan, and Professor Roothaan's generosity in making this program available is gratefully acknowledged.

APPENDIX

The Hartree-Fock and pseudonatural orbitals are linear combinations of basis functions,

$$\varphi_{nlm}=\sum C_{nl}{}^{i}\chi_i{}^{l,m},$$

where the basis functions $\chi_i{}^{l,m}$ are Slater-type orbitals,

$$\chi_i{}^{l,m}=(2\zeta)^{p_i+1/2}[(2p_i)!]^{-1/2}r^{p_i-1}e^{-\zeta_i r}Y_l{}^m(\nu,\varphi).$$

TABLE VI. The basis set and orbital coefficients for Na^-.

p	ζ	$1s$	$2s$	$3s$	$4s$	$5s$
1	9.44	0.91840	−0.30885	0.03275	0.04923	−0.05665
1	15.95	0.13361	0.00584	−0.00075	−0.00150	0.00084
2	4.384	0.00152	0.49225	−0.06376	−0.08041	0.14479
2	2.812	0.00064	0.61160	−0.05960	−0.10672	0.07166
3	11.624	−0.05820	−0.02416	0.00488	0.00358	−0.01640
3	0.966	−0.00004	0.00091	0.50577	0.97785	−1.83528
3	0.419	0.00002	−0.00025	0.63333	−1.37311	−4.45079
3	0.53	0.0	0.0	0.0	0.44599	5.76493
p	ζ	$2p$	$3p$	$4p$		
2	3.267	0.49583	−0.05047	0.04575		
2	2.069	0.34366	−0.04494	0.27964		
2	12.05	0.00774	−0.00079	0.00071		
2	5.703	0.23222	−0.02364	0.02143		
3	0.99	0.0	0.17398	−1.71334		
3	0.57	0.0	0.86726	1.37622		
p	ζ	$3d$	$4d$			
3	0.85	1.37042	2.01106			
3	1.3	−0.50428	−3.23353			
3	2.0	0.07187	1.02768			
p	ζ	$4f$				
4	0.75	1.0				

TABLE VII. The SOC wave function for Na^-.

Configurations	Coefficients
$3s^2$	0.94108
$3s4s$	0.07418
$4s^2$	−0.11780
$3s5s$	0.03817
$5s^2$	−0.00578
$3p^2$	−0.30503
$4p^2$	−0.00992
$3d^2$	−0.01742
$4d^2$	−0.00297
$4f^2$	−0.00677

The basis functions and orbitals for Na^- are given in Table VI, and the final SOC wave function constructed from these orbitals is given in Table VII.