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Independent-particle models for light negative atomic ions

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For the purposes of astrophysical, aeronomical, and laboratory application, we seek a precise independent-particle model for electrons in negative atomic ions of the second and third period. The optimum-potential model (OPM) of Talman *et al.* is first used to generate numerical potentials for eight of these ions. Results for total energies and electron affinities are found to be very close to Hartree-Fock solutions. However, the OPM and HF electron affinities both depart significantly from experimental affinities. For this reason we develop two analytic potentials whose inner energy levels are very close to the OPM and HF levels but whose last electron eigenvalues are adjusted precisely with the magnitudes of experimental affinities. These models are (1) a four-parameter analytic characterization of the OPM potential and (2) a two-parameter potential model of the Green, Sellin, Zachor type. The system O^- or e-O, which is important in upper atmospheric physics is examined in some detail.

I. INTRODUCTION

Negative ions play important roles in astrophysical, aeronomical, and laboratory phenomena.[1-4] For example, H^- is the major source of opacity in the continuum of the sun and many stars and plays a part in many stellar reactions. The negative ions O^- and O_2^- and others in the earth's upper atmosphere have important effects in determining the density of free electrons which influence radio communications and other aeronomical phenomena. In the laboratory, negative ions influence radiation from shock waves, the shape of gaseous discharge pulses, and other experimental observations. Negative ions are used in tandem Van de Graaff accelerators for multiplying the energy of the accelerated particles. While the abundance of negative ions is usually small compared to neutrals, the fact that they are charged and that electron affinities are small often amplifies their influence.

The independent-particle model (IPM) of electrons in central potentials within atoms provides a simple atomic model for describing negative ions. Here the physical results are all extracted from a radial Schrödinger equation of the form

$$-\phi''(r)+[V(r)+l(l+1)/r^2]\phi(r)=E\phi(r)\,, \qquad (1)$$

where $V(r)$ is the electron-atom potential. We use units so that $2m=\hbar=\frac{1}{2}e^2=1$, in which case radial distances are in Bohr radii and the energy eigenvalues (E) are in rydberg units.

Green, Sellin, and Zachor[5] (GSZ) have introduced an IPM which, for the case of an electron in a negative ion, takes on the form

$$V=-(2Z/r)\Omega(r)\,, \qquad (2)$$

where $\Omega(r)$ is the two-parameter (H and d) screening function

$$\Omega(r)=[H(e^{r/d}-1)+1]^{-1}\,. \qquad (3)$$

In attempting to fix the GSZ parameters for negative atomic ions we first considered the approach of Bass, Green, and Wood[6] (BGW) in which the parameters of the analytic GSZ model were determined by minimizing the expectation of the Hartree-Fock Hamiltonian with respect to a Slater determinant wave function constructed from one-electron wave functions in a GSZ-type potential. These parameters may be obtained from Table I of Garvey *et al.*[7] by extrapolating the parameters for various isoelectronic sequences to the case $N=Z+1$. Unfortunately, the two parameters so obtained did not always lead to the binding of the last electron. It should be noted, however, that the optimum potential obtained by minimizing the total energy is not necessarily the best IPM potential for atomic-shell and optical-model calculations. This question has already been discussed in comparative studies by Green and Kutcher[8] and Talman, Ganas, and Green[9] (TGG). In this regard negative atomic ions are of particular interest since they provide extreme cases to examine the question of the most appropriate potential from the viewpoint of an IPM description of an atomic system. In the case of negative ions we do not have excited states or experimental data on inner bound states, so the adjustment technique of Ganas and Green[10] cannot be directly applied. The precise Roothaan Hartree-Fock descriptions of Clementi and Roetti[11] are available, but in such a model each electron implicitly "sees" its own unique potential. To overcome this problem we have treated light negative ions by the numerical optimized potential of Talman *et al.*[12-15]

II. OPTIMIZED-POTENTIAL MODEL

In this section an approach (to be referred to as

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the OPM) for constructing an average effective potential that is closely related to the Hartree-Fock method will be taken.[12] Unlike the BGW analytic approach, here the Hartree-Fock energy functional is minimized with respect to a numerical effective potential. The resulting wave functions have been shown[13] to give results almost the same as Hartree-Fock results for many physical quantities.

It was shown in Ref. 12 that for a closed-shell atom the variationally optimized effective potential $V(r)$ satisfies an integral equation of the form

$$\int_0^\infty H(r,r')[V(r')-V_H(r')]dr' = Q(r)\,, \tag{4}$$

where

$$H(r,r') = \sum_i n_i\phi_i(r)G_i(r,r')\phi_i(r')\,, \tag{5}$$

$$Q(r) = -\sum_{ij} n_i n_j \int_0^\infty dr'\,\phi_i(r)G_i(r,r')\phi_i(r')\sum_L \begin{pmatrix} l_i & l_j & L \\ 0 & 0 & 0\end{pmatrix}^2 \int_0^\infty dr''\,\frac{\min(r',r'')^L}{\max(r',r'')^{L+1}}\,\phi_i(r'')\phi_j(r'')\,. \tag{6}$$

In these equations, $\phi_i(r)$ is the reduced radial wave function in shell i, to be determined self-consistently, and n_i is the occupation number of shell i. The functions $\phi_i(r)$ satisfy the reduced radial Schrödinger equation [Eq. (1)]. In Eq. (4), $V_H(r)$ is the static Hartree potential produced by the electron charge distribution, and in Eqs. (5) and (6) $G_i(r,r')$ is the Green's function for the Schrödinger equation calculated at $E=E_i$ and projecting onto states orthogonal to ϕ_i. We may write the potential $V_p(r)$ in the form

$$V(r) = V_p(r) - 2Z/r\,, \tag{7}$$

where $-2Z/r$ is the attractive potential arising from the nucleus, and $V_p(r)$ physically represents the interaction of the electron cloud with the individual electron allowing for electron static and average exchange effects.

If the atom or ion has an open shell there are extra terms in $Q(r)$ which arise from constructing the ground-state eigenfunctions of L^2 and S^2. It turns out from Hund's rules[14] that these terms can be calculated fairly simply for the ground state by forming the wave function with the largest values of m_L and m_s, which is a single Slater determinant.

It was shown in Ref. 12 that for an atom the effective potential behaves like $-2/r$ for large r; i.e., at large r an electron moves in the potential of the ion it leaves behind. For a negative ion, since a neutral atom is left behind, the effective potential should clearly approach zero more rapidly than r^{-1}.

The above result can be demonstrated by arguing that for large r, Eq. (4) is dominated by the terms in H and Q for which $i=v$, where v refers to the least bound valence electron. At large r, a factor $n_v\phi_v(r)$ can then be divided out of Eq. (6) and the integral operator $G_v(r,r')$ inverted by a differential operator. The result is then

$$\phi_v(r)[V(r)-V_H(r)] = -\sum_j n_j\phi_j(r)\sum_L \begin{pmatrix} l_v & l_j & L \\ 0 & 0 & 0\end{pmatrix}^2 \int_0^\infty dr'\,\frac{\min(r,r')^L}{\max(r,r')^{L+1}}\,\phi_j(r')\phi_v(r')\,. \tag{8}$$

At large r values, the term $j=v$ dominates the sum on the right-hand side. It is then found that for large r

$$V(r)-V_H(r) = -n_v\sum_L \begin{pmatrix} l_v & l_v & L \\ 0 & 0 & 0\end{pmatrix}^2 \int_0^\infty dr'\,\frac{\min(r,r')^L}{\max(r,r')^{L+1}}\,\phi_v(r)^2\,. \tag{9}$$

The term $L=0$ gives rise to the term in $-2/r$ mentioned above and in the negative-ion case is canceled. Unless the valence state is an s state the dominant term in Eq. (9) for a negative ion is $L=2$, and this gives rise to an r^{-3} potential. This argument would be changed in detail but would remain valid in the open-shell case.

Using these procedures, numerical optimized effective potentials have been calculated for the negative ions B^-, C^-, N^-, F^-, Si^-, P^-, S^-, and Cl^-. It was apparently not possible to obtain results for which the outer electron is bound for the ions Li^-, Na^-, and Al^-, although it is possible that a satisfactory starting approximation was not found.

The results for the total energies, electron affinities, and least bound-particle eigenvalues are given in Table I. Here the electron affinities are calculated by subtracting the energies of the corresponding atoms calculated in the OPM.[15] The results are compared with the Hartree-Fock re-

TABLE I. Total energies and electron affinities in rydbergs for negative ions calculated in the OPM and the Hartree-Fock approximation. E, total energy; ϵ, electron affinity; E_{HF}, Hartree-Fock total energy; ϵ_{HF}, Hartree-Fock electron affinity; ϵ_{expt}, observed electron affinity.[a] $|E_v|$ is the magnitude of the valence-electron eigenvalue for the OPM.

Ion	E	ϵ	$E_{(\mathrm{HF})}$	$\epsilon_{(\mathrm{HF})}$	ϵ_{expt}	$\lvert E_v\rvert$
B$^-$	−49.0360	−0.0195	−49.0384	−0.0197	0.0206	0.0505
C$^-$	−75.4132	0.0402	−75.4176	0.0404	0.0932	0.1485
N$^-$	−108.6404	−0.1560	−108.6438	−0.1580		
O$^-$	−149.5762	−0.0387	−149.5790	−0.0397	0.1075	0.2540
F$^-$	−198.9156	0.0999	−198.9187	0.1001	0.2499	0.3560
Si$^-$	−577.7705	0.0697	−577.7789	0.0703	0.1018	0.1196
P$^-$	−681.3888	−0.0376	−681.3973	−0.0401	0.0546	0.1508
S$^-$	−795.0675	0.0677	−795.0764	0.0667	0.1527	0.2111
Cl$^-$	−919.1439	0.1870	−191.1534	0.1897	0.2658	0.2950

[a] Reference 4.

sults of Clementi and Roetti,[11] with the electron affinities calculated in the corresponding way. Also shown are the magnitudes of the eigenvalue $|E_v|$ of the last electron in the OPM.

It is seen that neither the OPM nor the HF results reproduce the experimental electron affinities. Differences in sign and factor of 2 differences in magnitude are seen in comparisons of ϵ(expt) with ϵ(OPM) and ϵ(HF). Perhaps the use of unrestricted Hartree-Fock wave functions would be more successful in reducing the total negative-ion energy; however, the use of such wave func-

TABLE II. Energy eigenvalues (in Ry) of negative atomic ions in the second period. For each ion the first row gives the configuration-averaged Hartree-Fock values of Clementi *et al.* The other rows correspond to the various calculations of this work.[a] The potential parameters d, H, α, and r_p are given, where applicable.

Ion	d	H	α	r_p	$1s$	$2s$	$2p$
Li$^-$	[$Z=3$, $\epsilon(\mathrm{expt})=0.0456$]				− 4.6455	−0.0291	
OPM							
AOP							
AAO							
GSZ	3.2227	4.4779			− 3.744	−0.0456	
B$^-$	[$Z=5$, $\epsilon(\mathrm{expt})=0.0206$]				−14.888	−0.5114	−0.0319
OPM					−13.073	−0.4495	−0.0505
AOP	1.8443	3.3567	5.588	2.6757	−12.669	−0.4318	−0.0519
AAO	1.8629	3.2446	5.588	3.9636	−12.837	−0.3890	−0.0206
GSZ	2.2920	4.0289			−12.783	−0.3907	−0.0206
C$^-$	[$Z=6$, $\epsilon(\mathrm{expt})=0.0932$				−22.010	−0.8061	−0.0972
OPM					−19.795	−0.7524	−0.1485
AOP	1.5066	2.9602	4.441	2.3702	−19.365	−0.7326	−0.1515
AAO	1.5237	2.9012	4.441	3.7307	−19.490	−0.6631	−0.0932
GSZ	1.7065	3.2482			−19.497	−0.6657	−0.0932
O$^-$	[$Z=8$, $\epsilon(\mathrm{expt})=0.1075$]				−40.396	−1.6265	−0.2585
OPM					−37.259	−1.3416	−0.2540
AOP	0.8555	1.9159	1.788	1.5447	−36.934	−1.3110	−0.2539
AAO	0.8517	1.8821	1.788	3.0237	−36.775	−1.1381	−0.1076
GSZ	0.8860	1.9607			−36.757	−1.1408	−1.1075
F$^-$	[$Z=9$, $\epsilon(\mathrm{expt})=0.2499$]				−51.659	−2.1489	−0.3617
OPM					−48.04	−1.733	−0.356
AOP	0.6698	1.6214	2.002	1.2867	−47.690	−1.7019	−0.3573
AAO	0.6708	1.6011	2.002	1.5906	−47.611	−1.5802	−0.2500
GSZ	0.774	1.8563			−47.494	−1.5814	−0.2499

[a] OPM, optimized potential method; AOP, analytic representation of optimized potential; AAO, analytic optimized potential adjusted to experiment; GSZ, analytic IPM potential.

tions would be outside the framework of a potential model. It is, however, gratifying to see that the OPM results are in substantial agreement with the Hartree-Fock results. Indeed, the total energy differences between the two methods are comparable to those found in calculations for atoms,[15] ranging from 50 ppm down to about 10 ppm as Z increases from 4 to 17. Furthermore, the agreement between the calculated electron affinities in the HF and OPM methods is remarkably good. These results confirm the discussion of TGG which suggests that the numerical OPM is probably the best "average" IPM representation of Hartree-Fock levels.

Comparison of $|E_v|$ for the OPM with ϵ(expt) also shows substantial differences all in the direction of excessive binding if the magnitude is to represent the removal energy or affinities. It would be desirable to adapt the OPM numerical potential for shell-type calculations in which $|E_v| = \epsilon$(expt). Such a modification would also set the stage for optical-model uses.

III. PARAMETRIZED IPM POTENTIALS FOR NEGATIVE IONS

We have found that the numerical OPM electron cloud–electron potentials that were calculated in Sec. II can be fitted by analytic potentials of the form

$$V_{\mathrm{ap}}(r) = 2(N-1)\Upsilon(r)/r + \alpha(r_p^2 + r^2)^{-3/2}, \tag{10}$$

$$\Upsilon(r) = 1 - 1/[1 + H(e^{r/d} - 1)]. \tag{11}$$

The first term in Eq. (10) follows from the analytic IPM of Green, Sellin, and Zachor.[5] The function $\Upsilon(r)$ behaves like Hr/d at small r and approaches 1 at large r. The second term in Eq. (10) is included to represent the r^{-3} behavior in the effective exchange potential derived in the previous section. Overall, $V_{\mathrm{ap}}(r)$ approaches a constant at $r = 0$ and behaves like $(N-1)2/r + \alpha r^{-3}$ for large r.

The parameter α in $V_{\mathrm{ap}}(r)$ was calculated from the large r behavior of the numerical OPM potentials. The other parameters H, d, and r_p were

TABLE III. Energy eigenvalues (in Ry) of negative atomic ions in the third period. See caption to TABLE II.

Ion	d	H	α	r_p	$1s$	$2s$	$2p$	$3s$	$3p$
Na^-	[Z=11, ϵ(expt) = 0.0401]				−80.663	−5.300	−2.742	−0.0250	
OPM									
AOP									
AAO									
GSZ	1.0142	2.1060			−83.222	−6.242	−4.451	−0.0401	
Al^-	[Z=13, ϵ(expt) = 0.0338]				−116.645	−9.462	−6.079	−0.4410	−0.0268
OPM									
AOP									
AAO									
GSZ	2.1187	6.3557			−109.15	−8.313	−5.565	−0.4029	−0.0338
Si^-	[Z=14, ϵ(expt) = 0.1018]				−137.163	−11.848	−8.050	−0.6409	−0.0783
OPM					−130.730	−10.109	−6.867	−0.5643	−0.1196
AOP	1.8043	5.7928	10.26	3.5979	−127.02	−9.798	−6.615	−0.5595	−0.1072
AAO	1.3357	4.0804	10.26	2.5674	−129.48	−10.232	−7.109	−0.5689	−0.1019
GSZ	2.1424	6.7362			−128.10	−10.147	−6.999	−0.5712	−0.1018
P^-	[Z=15, ϵ(expt) = 0.0546]				−159.401	−14.480	−10.262	−0.8831	−0.1409
OPM					−152.46	−12.559	−8.925	−0.7224	−0.1508
AOP	1.5762	5.0041	3.927	2.765	−150.34	−12.340	−8.818	−0.7044	−0.1406
AAO	1.4727	4.5907	3.927	7.566	−151.10	−12.325	−8.834	−0.5882	−0.0548
GSZ	1.5053	4.7156			−150.84	−12.281	−8.784	−0.5888	−0.0546
S^-	[Z=16, ϵ(expt) = 0.1527]				−183.352	−17.350	−12.710	−1.159	−0.2148
OPM					−175.92	−15.256	−11.226	−0.9132	−0.2111
AOP	1.1938	3.7996	4.152	1.7857	−175.13	−15.075	−11.206	−0.8943	−0.2067
AAO	1.2139	3.8467	4.152	2.2813	−175.07	−14.886	−11.022	−0.8138	−0.1529
GSZ	1.4674	4.7189			−174.17	−14.801	−10.911	−0.8159	−0.1527
Cl^-	[Z=17, ϵ(expt) = 0.2659]				−209.010	−20.458	−15.391	−1.466	−0.2998
OPM					−201.10	−18.202	−13.769	−1.132	−0.2950
AOP	1.0404	3.3809	3.457	1.3729	−200.83	−18.003	−13.758	−1.115	−0.2961
AAO	1.0338	3.3710	3.457	1.4093	−200.47	−17.825	−13.567	−1.074	−0.2658
GSZ	1.3071	4.1853			−201.08	−17.969	−13.758	−1.068	−0.2659

adjusted to minimize the quantities

$$S = \int_0^\infty [V(r) - V_{\mathrm{ap}}(r)]^2 r\,dr\,. \tag{12}$$

The factor r in Eq. (12) is one of many possible weight functions that could be used. It was found that of the weight functions 1, r, and r^2 this choice generated the $V_{\mathrm{ap}}(r)$ which gave the minimum total energies.

The parameters for the analytic-potential form $V_{\mathrm{ap}}(r)$ are given in the third rows of each block in Tables II and III. Also given are the energy eigenvalues. As expected these are very close to the OPM results. The total energies obtained from the AOP generally are 20–50 ppm greater than those of OPM except for B^- and C^-. To be consistent, the parameters should have been calculated as in Ref. 6 by the more complicated procedure of minimizing the Hartree-Fock energy rather than the quantity in Eq. (22). However, the differences given are comparable to those found[6] using the energy-minimization procedure.

The OPM effective potential for O^- is shown in Fig. 1 together with its parametrized analytic approximation. Evidently there is good agreement at all r values.

Our work to this point indicates that the electron affinities of negative ions do not agree with the energy differences computed using HF, the V(OPM) potential, or the four-parameter analytic approximation $V_{\mathrm{ap}}(r)$. Nor do the electron affinities equal the last particle eigenvalues. It must be recognized, however, that the last electron in a negative ion is in an extremely sensitive balance between a large negative potential energy and a large positive kinetic energy. Thus we are in a situation in which small residuals, including those not encompassed by an independent-particle model, can play a significant physical role. To obtain an IPM potential which gives the last particle eigenvalue in agreement with the electron affinity, we have utilized the analytic approximation to the optimum potential consisting of Eqs. (10) and (11) and adjusted the value of r_p (and in some cases d and H as well) so that e_v equals the electron affinity. The parameters so obtained are given in the fourth row of the blocks in Tables II and III. The changes in total energy obtained in this way were quite substantial in several cases, e.g., in O^- where it amounted to 1193 ppm.

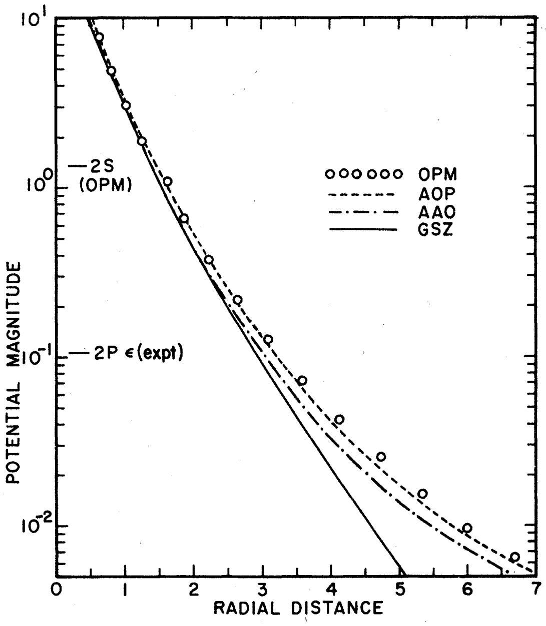

FIG. 1. Illustration for O^- of IPM potentials discussed in this work. OPM represents the numerical optimum potential; AOP is a four-parameter analytic approximation to OPM; AAO is an adjusted potential of the same form which gives the experimental affinity; and GSZ is a two-parameter potential which gives the experimental affinity and reasonable $2s$ and $1s$ eigenvalues.

For applications of interest the four-parameter analytic model described above may not be the most economical analytical IPM. We have therefore returned to the original two-parameter GSZ model for negative ions [see Eqs. (2) and (3)] to see if we can find reasonable parameter values which produce agreement between the last electron eigenvalue and the affinity, yet incorporate the inner features of the OPM. Here we have used the search procedure of Ganas and Green[10] to adjust the two parameters of the GSZ potential to fit the inner-state eigenvalues of the OPM and the experimental affinity for the last electron. We could alternatively have used inner eigenvalues of the Hartree-Fock results of Clementi and Roetti,[11] which are quite close to those of the optimized potential. The results are given in the fifth rows of Tables II and III. It is seen that the two-parameter analytic model can indeed be adjusted to give exact affinities and reasonable inner-state eigenvalues.

We are now in a position to take advantage of the flexibility of the analytic GSZ potential to deal with the problem ions such as Li^-, Na^-, and Al^- whose last electron could not be bound with the optimized potential. Parameters which give reasonable properties are also given in Tables II and III. Cases of unstable negative ions such as Be^- and N^- can also be accommodated by this approach. For example, by interpolating the H value between the neighboring negative ions and adjusting the d value we find that $H = 4.25$ and $d = 2.90$ gives $|E_{\hat{v}}| \approx 0$ for Be^-, and $H = 2.60$ and $d = 1.20$ gives $|E_{\hat{v}}| \approx 0$ for N^-. GSZ potentials with these parameters or with slightly smaller values of *d* should provide reasonable representations of the *e*-Be and *e*-*N* systems.

IV. DISCUSSION AND CONCLUSIONS

The relationship between the single-particle eigenvalues and the ground-state energies of negative ions is a matter of considerable interest. As is well known,[4] fine-structure splittings of a multielectron configuration such as $(2p)^n$ will stabilize particular angular-momentum states with respect to the orbital center of gravity. Thus the experimental affinity of the ground state should in general be larger than the single-particle orbital energy. The fact that the unadjusted OPM or AOPM already have single-particle eigenvalues which are larger than experimental affinities gives further support to the adjustment process used in the AAO and GSZ models. However, it should be noted then that these adjusted potentials then empirically include effects which go beyond the single-particle model.

The magnitude of these effects are discussed by Hotop and Lineberger.[4] For example, for the $(2p)^6$ state of F^- the ${}^1S_0$ state is not split. For the $(2p)^5$ state of O^- the spin-orbit splitting between the ground ${}^2P_{3/2}$ state and the excited ${}^2P_{1/2}$ state is small, $\approx 181\ \mathrm{cm}^{-1} \approx 1.65\times 10^{-3}$ Ry. For the $(2p)^4$ N^- the term splittings calculate to be of the order of 1.4 eV for $N({}^3P - {}^1D)$ and 3 eV for $N({}^3P - {}^1S)$. For $(2p)^3C^-$ the multiplet splittings are also approximately 1 eV. Thus one must expect that adjustments of the order of 1 eV or 0.1 Ry associated with multiplet splittings are incorporated in the AAO and GSZ potentials.

From a more theoretical point of view the relationship of the single-particle eigenvalue and the electron affinity must consider the detailed perturbation treatment used to go from the IPM to a more accurate many-electron treatment. It must be recognized, however, that the calculation of atomic-electron affinities is a very difficult and largely neglected subject.[16] The very weak binding of negative ions greatly enhances the importance of many otherwise small effects. For example, Moser and Nesbet,[17] using Bethe-Goldstone equations to calculate electron affinities of light negative ions, find an overestimate of the stability when only one- and two-particle terms are included. The three-particle terms which are all positive in sign reduce these affinities, but they are very numerous and costly to compute.

Sasaki and Yoshimine,[18] using the configuration-interaction (CI) method, appear to obtain 94–95% of the true correlation energy for second-period ions. However, because of wave-function inaccuracies their electron affinities turned out to be only 83% of the true contribution. Nevertheless, CI calculations using basis sets built up progressively look quite promising.

For the purposes of applications in which wave functions in a reasonable potential are needed, the adjusted analytic-potential method appears to be a practical way of tuning the effective valence-state potential to electron affinity inferred from experiment or refined many-body calculations.

In such application it must be recognized that the parameters of the AAO or GSZ potential would be expected to have a slight state dependence which may or may not be consequential. For example, if these potentials are used as optical-model potentials to calculate 100-eV electron-atom elastic scattering such as carried out by Berg *et al.*[19] and Furness and McCarthy,[20] these differences should be of minor consequence. It was in connection with such calculations that this work was initiated.

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