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Calculated electron affinities of the elements

Lee A. Cole* and J. P. Perdew
Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118

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The extra-electron binding energies of the ground-state monatomic negative ions with $Z < 86$ are calculated using the self-interaction correction (SIC) to the local spin-density approximation (LSD) for exchange and correlation. The results agree reasonably with experiment, and the errors reflect the familiar "interconfigurational energy error" common to LSD and SIC. Some of the rare earths, e.g., Ce and possibly Gd, are predicted to form stable negative ions. In addition we have the following: (1) Relativistic (other than spin-orbit) contributions to the electron affinities are included and discussed. In Au the relativistic effects boost the calculated affinity from 1.5 to 2.5 eV. (2) The doubly negative ions O^{2-} and Te^{2-} are predicted to have no stable ground state. (3) Electron affinities are calculated for a few excited atomic states. (4) The calculated ground-state densities $n(r)$ of all the neutral atoms and negative ions are monotonically decreasing functions of r. (5) Corrections to the random-phase-approximation electron-gas correlation energy are shown to cancel out of SIC calculations for atoms.

I. INTRODUCTION

The electron affinity A of an atom is the energy released when an extra electron binds to the atom, forming a negative ion. This quantity, which obviously influences charge transfer in molecules and solids, enters Mulliken's definition of the electronegativity,[1]

$$\chi=\tfrac{1}{2}(I+A)\ , \qquad (1)$$

where I is the first ionization potential of the neutral atom. Isolated negative ions are also of interest, not only in the laboratory but also in outer space and in the Earth's upper atmosphere.[2-4]

Unlike many other atomic properties, the electron affinities are hard to calculate with a small relative error. The negative ions are so loosely bound that effects usually regarded as small, especially electron correlation, play a crucial role in binding them. Starting with the $3d$ transition series of the periodic table, relativistic effects also influence the affinities significantly.[5,6] While the affinities of most of the elements have been measured quite accurately,[3] e.g., by laser photodetachment, reliable calculations exist only for the lightest elements (say $Z \leq 17$).

The single-configuration Hartree-Fock approximation, which neglects correlation, gives a very poor description of the affinities.[6] The Hartree-Fock total energy differences *under*estimate the affinities so badly that, of the six stable negative ions with $Z \leq 9$, only two (carbon and fluorine) are predicted to be stable. On the other hand, the Hartree-Fock orbital energies usually *over*estimate the affinities. Recently, adjustment of the one-electron potential was proposed[7] to fit the orbital energies to experiment.

The method of configuration interaction includes correlation via the mixing of orbital configurations. Conscientious calculations[8] of electron affinities for B through F still disagree with experiment by 0.1 − 0.3 eV. Somewhat better agreement for Al through Cl has been obtained[9] by concentrating on valence-valence correlation and relying on a cancellation of error from the core. Calculations of this kind have been reviewed in several recent articles.[3,4,6]

Density functional approximations[10,11] have the potential to incorporate correlation *within* an orbital scheme that is similar to but simpler than single-configuration Hartree-Fock. For example, in the local spin-density (LSD) approximation[11,12] the exchange-correlation energy is

$$E_{\mathrm{xc}}^{\mathrm{LSD}}[n_\uparrow,n_\downarrow]=\int d^3r\, n(\vec{r})\epsilon_{\mathrm{xc}}(n_\uparrow(\vec{r}),n_\downarrow(\vec{r}))\ , \qquad (2)$$

where $\epsilon_{\mathrm{xc}}(n_\uparrow,\ n_\downarrow)$ is the exchange-correlation energy per particle of an electron gas with uniform spin densities $n_\uparrow$ and $n_\downarrow$. The density $n(\vec{r})=n_\uparrow(\vec{r})+n_\downarrow(\vec{r})$ is constructed from orbitals which feel the self-consistent potential

$$\frac{-Z}{r}+\int d^3r'\,\frac{n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}+\mu_{xc}^{\sigma}(n_\uparrow(\vec{r}),n_\downarrow(\vec{r}))\;, \qquad (3)$$

where

$$\mu_{xc}^{\sigma}(n_\uparrow,n_\downarrow)=\frac{\partial}{\partial n_\sigma}[n\epsilon_{xc}(n_\uparrow,n_\downarrow)] \qquad (4)$$

is a *local* exchange-correlation potential. Unfortunately, negative ions do not find self-consistent solutions within LSD or the related $X\alpha$ approximation.[13,14] Nevertheless, the affinities can still be estimated by artifice—e.g., by confining the negative ion inside a large spherical box,[13] or by applying Eq. (1) with Slater transition-state calculations of χ and I.[15] Direct calculations of A by the transition-state method have also been reported.[15,16]

LSD fails for the negative ions because Eqs. (2) and (4) include a spurious interaction of each electron with itself. In particular, for an N-electron ion the potential (4) tends to $(N-Z)/r$ at large r, and not to the electrostatically correct limit $(N-1-Z)/r$. There are several schemes[17–23] to remove the self-interaction from Eqs. (2) and (4), all of them permitting self-consistent solutions for negative ions ($N=Z+1$) and some of them[21–23] yielding reasonable estimates of the affinities. One[22,23] of the latter group which has been tested extensively[24–28] for neutral atoms as well as positive and negative ions is the self-interaction corrected (SIC) scheme:

$$E_{xc}^{\mathrm{SIC}}=E_{xc}^{\mathrm{LSD}}[n_\uparrow,n_\downarrow]-\sum_{\alpha\sigma}\left[\frac{1}{2}\int d^3r\int d^3r'\,\frac{n_{\alpha\sigma}(\vec{r})n_{\alpha\sigma}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}+E_{xc}^{\mathrm{LSD}}[n_{\alpha\sigma},0]\right]\;, \qquad (5)$$

where $n_{\alpha\sigma}(\vec{r})=|\psi_{\alpha\sigma}(\vec{r})|^2$ is an orbital density. The orbitals are constructed from the orbital-dependent exchange-correlation potential

$$\mu_{xc}^{\sigma}(n_\uparrow(\vec{r}),n_\downarrow(\vec{r}))-\left[\int d^3r'\,\frac{n_{\alpha\sigma}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}+\mu_{xc}^{\uparrow}(n_{\alpha\sigma}(\vec{r}),0)\right]\;. \qquad (6)$$

While these orbitals for different α are not strictly orthogonal, the effect of Schmidt orthogonalization upon the total energy is negligible, e.g., less than 0.01 eV for Kr.[25] In order to simplify the calculations, the orbital densities in Eqs. (5) and (6) are replaced by their spherical averages.

In this paper we report SIC calculations of the electron affinities of the elements. We emphasize that the SIC approximation is simple, fully self-consistent, and involves no empirical input. Because the affinity is calculated as the small difference of two large numbers, the total energies of the neutral atom and negative ion must be well converged. To insure this, we used an "energy norm"

$$\int d^3r\left|\frac{\delta E}{\delta n(\vec{r})}\Delta n(\vec{r})\right| \qquad (7)$$

to monitor the difference $\Delta n(\vec{r})$ between input and output densities on each iteration. Details of this idea will be presented elsewhere.[29] (Some other methods of calculating electron affinities avoid the need to take the small difference of two large energies—e.g., the transition-state[15,16] and many-body Green's-function[30] methods.)

Because correlation is important, we have used a parametrization[25] of $\epsilon_c(n_\uparrow,\,n_\downarrow)$ which accurately describes the true electron-gas correlation energy. However, we have found (Appendix A) that essentially the same SIC values for the total energies *and* affinities would be found using the simple random-phase approximation (RPA) for the electron-gas correlation-i.e., corrections to the RPA essentially cancel out of (5) and (6). This behavior supports a recent suggestion[31] that the RPA might be much better for atoms than it is for the electron gas.

Unlike earlier SIC calculations[24,25] for the electron affinities of some lighter atoms, these calculations are relativistic. Because the LSD and SIC approximations assume that σ (the z component of electron spin) is a good quantum number, these approximations do not blend well with the full Dirac one-electron equation. We solve instead the Koelling-Harmon equation,[32] equivalent to the Dirac equation with the spin-orbit interaction averaged out. The electron-gas exchange energy ϵ_x $(n_\uparrow,$ $n_\downarrow)$ also includes a relativistic correction,[33,34] although this has little effect on the affinities. The relevant expressions are collected in Appendix B. We also performed a few calculations in the nonrelativistic limit with the same computer program in order to gauge the relativistic contributions.

II. RESULTS

A. Electron affinities of atomic ground states

The calculated affinities are compared with measured values for $Z < 86$ in Fig. 1. The neutral atom and negative ion orbital configurations were taken from the review article by Hotop and Lineberger,[3] as were most of the experimental affinities except for a few more recent values.[35–38]

The calculated values are in satisfactory agreement with experiment, and the discrepancies exhibit patterns which are not hard to understand. Consider, for example, $Z < 36$. The calculated affinities for s electrons are nearly exact, while those for p electrons are about 0.3 eV too large. The calculated affinities for $3d$ electrons are also too large, sometimes by more than 1 eV but with considerable scatter.

These errors just reflect the familiar "interconfigurational energy error"[39] which shows up in both[25,26,28] LSD and SIC calculations of ionization potentials for the *neutral* atoms. The calculated removal energies are about right for s electrons, a little too large for p electrons, and about 1 eV too large for $3d$ electrons. The $3d$ errors are scattered due to the spherical averaging (which can be removed with some extra effort).[40]

Discrepancies between theory and experiment are no worse for the heavier atoms ($Z > 36$) and, in fact, the errors of the calculated affinities for $4d$ electrons are somewhat smaller than for $3d$ electrons, again mimicking the errors of the LSD interconfigurational energies of the neutral atoms.[39]

B. Affinities of the rare earths

Hotop and Lineberger[3] have observed that "Almost nothing is known about the negative ions of the rare-earth elements."

Recently Sen, Schmidt, and Weiss[41] have used Eq. (1) and the relativistic $X\alpha$ method to estimate the electron affinities of the rare earths. They found *negative* affinities around -4 eV and concluded that these negative ions are "not likely to be stable."

However, an earlier semiempirical estimate by Zollweg[42] predicted small *positive* affinities for at least four of the rare earths (Ce, Pr, Nd, and Gd). We have performed calculations for these four negative ions, assuming a configuration the same as that of the neutral atom plus one extra $5d$ electron. The resulting affinities are compared with Zollweg's estimates in Table I. The agreement is about as good as could be expected and tends to support Zollweg's analysis.

The neutral atom configurations[43] are $4f^{k-3}\,5d^1\,6s^2$ for Ce and Gd, and $4f^{k-2}\,5d^0\,6s^2$ for Pr and Nd. The calculated affinities are significantly smaller for the latter configuration, probably be-

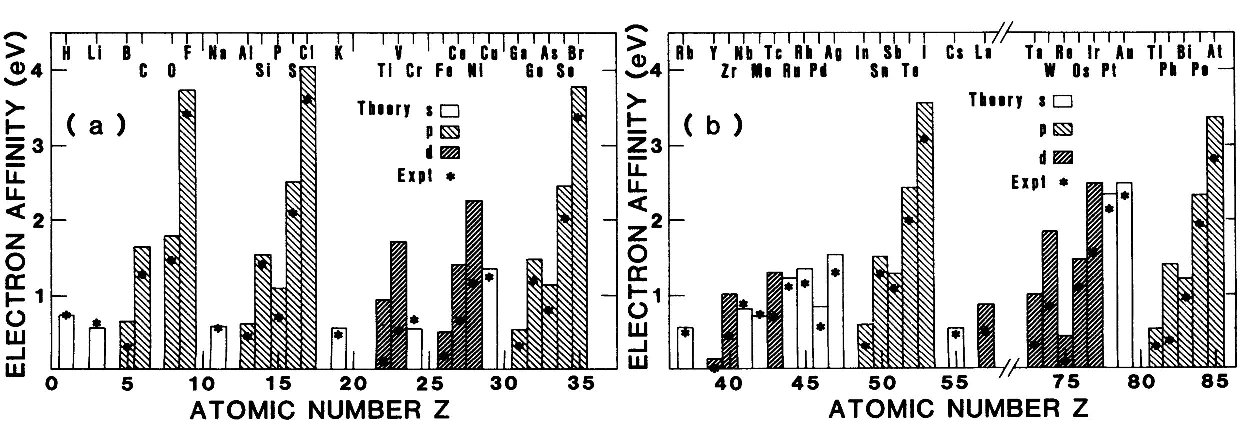

FIG. 1. Theoretical (histogram bars) and experimental (asterisks) electron affinities of the elements for (a) $Z < 36$ and (b) $Z > 36$. Cross hatching indicates the angular momentum of the electron added to form the negative ion. [Experimental values from Ref. 3, with the exception of more recent values for Al, Pb, Bi (Ref. 37); Ti, V, Cr, Zr, Nb, Mo, Rh, Pd, Ta, W, Ir (Ref. 38); Fe (Ref. 35); and Co, Ni (Ref. 36).]

TABLE I. Calculated electron affinities of the rare earths, compared with semiempirical estimates of Zollweg (Ref. 42). Since our theory tends to exaggerate the affinities for 5*d* electrons, we are skeptical about the existence of stable Pr^- and Nd^-, where the calculated affinities are only 0.1 eV (and where the calculated 5*d* orbital energies of the negative ions are essentially zero).

		Electron affinity (eV)	
Atom	Z	This work	Zollweg
Ce	58	0.81	0.6
Pr	59	0.11	0.3
Nd	60	0.10	0.1
Gd	64	0.34	0.2

cause 4*f* electrons shield the nuclear potential more efficiently than 5*d* electrons.

C. Relativistic contributions to the affinities

Table II shows the calculated relativistic (excluding spin-orbit) contribution to the electron affinity for selected atoms. For those atoms with $Z < 36$, this table also exhibits the same quantity as calculated by Fraga, Saxena, and Lo.[5] Unlike the present work, their calculation employed *nonrelativistic* orbitals to evaluate the expectation values of the mass-enhancement and Darwin operators.

It appears from Table II that relativity *enhances* the affinity for *s* electrons (as in the alkali and noble metals) and *suppresses* the affinity for *p* (as in the halogens) and *d* electrons (as in the transition metals). The relativistic effects are small in the alkalis and halogens, but dramatic in the transition and noble metals.

TABLE II. Calculated relativistic (excluding spin-orbit) contributions to the electron affinities of selected atoms. Unlike this work, the calculation of Fraga *et al.* (Ref. 5) employed *nonrelativistic* orbitals of the *analytic* Hartree-Fock-Clementi form to evaluate the expectation values of the mass enhancement and Darwin operators.

		(eV)	
Atom	Z	This work	Fraga *et al.*
K	19	0.00	−0.00
Rb	37	0.01	
Cs	55	0.02	
Cu	29	0.07	−0.00
Ag	47	0.22	
Au	79	1.03	
Cl	17	−0.01	0.06
Br	35	−0.04	−0.05
I	53	−0.06	
At	85	−0.21	
Fe	26	−0.22	−0.27
Os	76	−1.52	

Fe can bind an extra 3*d* electron and relativistic effects reduce its affinity by 0.2 or 0.3 eV. Bunge and Bunge[6] have attributed this reduction to a substantial outward relaxation of the valence orbitals that occurs when the extra electron is bound.

Both Cs and Au can bind an extra 6*s* electron, but in Au the 6*s* orbital is considerably more contracted and feels a much stronger nuclear potential. The relativistic contribution to the electron affinity of Au is a full electron volt, which is comparable to the contribution from correlation and essential to the agreement between theory and experiment. Note that, in the absence of relativistic effects, gold and silver would have similar electron affinities, as discussed qualitatively by Pyykkö and Desclaux[44]; it is relativity which makes gold "almost a halogen."

D. Monotonic ground-state densities

The atomic ground-state densities $n(r)$ are monotonically decreasing functions of r. [It is only $4\pi r^2 n(r)$ which exhibits the familiar shell-structure oscillations.] Weinstein, Politzer, and Srebrenik[45] pointed out this fact for the neutral atoms with $Z \leq 36$. Our computer program checked the calculated ground-state densities of all the neutral atoms *and* negative ions with $Z \leq 86$, and found that they are always monotonic. There could be a theorem here in search of a proof.

E. Doubly negative ions

Mass spectrometric observations of doubly charged negative ions, including O^{2-}, Te^{2-}, F^{2-}, Cl^{2-}, Br^{2-}, and I^{2-} have been reported,[46] although these observations have not been confirmed by other groups.[46]

We could not have checked all the possible excited states that might be doubly negative, but we did search for ground-states of O^{2-} and Te^{2-}. Here the neutral atom valence configuration is p^4, with a fairly substantial affinity for the first extra electron, so a second extra electron might be welcome to complete the *p* subshell. However, we found that the SIC equations have no self-consistent bound solutions for O^{2-} or Te^{2-} in the p^6 configuration, and we strongly suspect that such ions do not exist. Herrick and Stillinger[47] have arrived at similar theoretical conclusions about O^{2-} using variational many-electron wave functions.

Out of curiosity, we took the ten-electron neon configuration and the nine-electron fluorine configuration, and continuously reduced the nuclear charge Z for each. The ten-electron configuration became energetically unstable against emission of an electron at $Z=8.73$, just as Herrick and Stillinger[47] predicted, although the $2p$ orbital energy of the ten-electron configuration did not go to zero until $Z=8.5$. These results suggest that O^{2-} ($Z=8$) is not very close to stability.

F. Electron affinities of excited states

Excited states of neutral atoms may also bind an extra electron, with the electron affinity defined as the total energy difference between excited neutral parent and negative daughter. The daughter, an excited state of the negative ion, might then decay by autodetachment, e.g., to the neutral ground state by emission of the extra electron.

The SIC equations admit excited-state solutions and have already been used to calculate the energies of the $(ns)^2$ autodetaching states of H^-.[48] Without any intention of making an exhaustive study of the affinities of excited states, we present a few typical results for light atoms in Table III.

III. CONCLUSIONS

The electron affinities of the elements (binding energies of the negative ions), including the important effects of correlation and relativity, have been calculated using the self-interaction correction to the local spin-density approximation for exchange and correlation. The results are in reasonable agreement with experiment and the absolute errors depend on the orbital character of the extra electron in much the same way as do the errors of the LSD and SIC ionization potentials for the neutral atoms. Some of the rare-earth atoms, e.g., Ce and possibly Gd, are predicted to form stable negative ions by binding an extra $5d$ electron.

Relativistic effects (excluding spin-orbit interaction) enhance the affinity for s electrons and suppress it for p and d electrons. These effects are small in the alkalis and halogens, but surprisingly large in the transition and noble metals. In gold, relativity boosts the calculated electron affinity from 1.5 to 2.5 eV.

The calculated ground-state electron densities of all the neutral atoms and negative ions are monotonically decreasing functions of distance from the nucleus. No stable ground state is predicted for the doubly negative ions O^{2-} and Te^{2-}.

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TABLE III. Electron affinities of some excited states of light atoms. [For C, only the daughter, and not the parent, is an excited state. No SIC solution was found for He^-. Sources of the experimental values are listed in Ref. 3. A few of the Expt. numbers are actually the results of sophisticated calculations: H (sources listed in Ref. 48) and Li (Ref. 51).]

		Electron affinity (eV)	
Parent	Daughter	Theory	Expt.
H $(2s\uparrow)^1$	H^- $(2s)^2$	0.40	0.63
$(3s\uparrow)^1$	$(3s)^2$	0.24	0.36
He $(1s\uparrow)^1(2s\uparrow)^1$	He^- $(1s\uparrow)^1(2s\uparrow)^1(2p\uparrow)^{1'}$		0.08
Li $(1s\uparrow)^1(2s\uparrow)^1(2p\uparrow)^1$	Li^- $(1s\uparrow)^1(2s\uparrow)^1(2p\uparrow)^2$	0.69	0.50
Be $(1s)^2(2s\uparrow)^1(2p\uparrow)^1$	Be^- $(1s)^2(2s\uparrow)^1(2p\uparrow)^2$	0.46	0.24
C $(1s)^2(2s)^2(2p\uparrow)^2$	C^- $(1s)^2(2s)^2(2p\uparrow)^2(2p\downarrow)^1$	0.10	0.04
N $(1s)^2(2s)^2(2p\uparrow)^2(2p\downarrow)^1$	N^- $(1s)^2(2s)^2(2p\uparrow)^2(2p\downarrow)^2$	1.58	1.0(3)

APPENDIX A: ON THE RANDOM-PHASE APPROXIMATION FOR ATOMS

The SIC correlation energy[23,25,27] is

$$E_c^{\mathrm{SIC}} = \int d^3r\, n(\vec{r})\epsilon_c(n_\uparrow(\vec{r}),n_\downarrow(\vec{r})) - \sum_{\alpha\sigma} \int d^3r\, n_{\alpha\sigma}(\vec{r})\epsilon_c(n_{\alpha\sigma}(\vec{r}),0)\,, \tag{A1}$$

where $\epsilon_c\ (n_\uparrow,\ n_\downarrow)$ is the correlation energy per particle of a uniform electron gas. Our SIC calculations have been performed using a parametrization[25] of the accurate Ceperley-Alder[49] ϵ_c. Remarkably, almost the same results would be obtained using a parametrization (Table IV) of the numerical RPA correlation energy $\epsilon_c^{\mathrm{RPA}}$.[50] For example, for Na we find a correlation energy per electron of -1.12 eV and an electron affinity of 0.59 eV using Ceperley-Alder, and -1.13 eV and 0.57 eV, respectively, using RPA.

It is not hard to see how the corrections to RPA cancel out of the correlation energy per electron in atoms, since the latter is dominated by high-density electrons and in the high-density limit[25]

$$\epsilon_c(n_\uparrow,n_\downarrow) = \epsilon_c^{\mathrm{RPA}}(n_\uparrow,n_\downarrow) + 0.63\ \mathrm{eV}\,. \tag{A2}$$

The second-order exchange constant, 0.63 eV, obviously cancels out of (A1) [but not out of the LSD correlation energy, the first term of (A1)]. What is more remarkable is that the corrections to RPA also cancel out of the electron affinity, a property of the low-density valence electrons.

APPENDIX B: RELATIVISTIC EXPRESSIONS

We self-consistently solve the one-electron radial equations of Koelling and Harmon[32]:

$$\phi' = -\frac{2}{r}\phi + \left[\frac{l(l+1)}{2Mcr^2} + \frac{1}{c}(V-E)\right] g\,, \tag{B1}$$

$$g' = 2Mc\phi\,, \tag{B2}$$

for each principal quantum number n, orbital angular momentum l, and spin σ, where

$$M = m + \frac{1}{2c^2}(E-V) \tag{B3}$$

is the relativistic mass, E is the orbital energy (excluding the rest energy mc^2), and V is the one-electron potential consisting of the first two terms of (3) plus (6). The spherically averaged orbital density, which integrates to 1 over all space, is

$$\frac{1}{4\pi}\left[g^2 + \phi^2 + \frac{l(l+1)}{(2Mcr)^2}g^2\right]. \tag{B4}$$

Only the large component g survives in the limit $c \to \infty$.

TABLE IV. Parameters for the RPA correlation energy of an unpolarized (*U*) and fully spin-polarized (*P*) electron gas. These parameters are to be used with the analytic expressions given in Appendix C of Ref. 25. The parameters were found by fitting these expressions to numerical RPA values (Ref. 50).

	U	P
A	0.0311	0.01555
B	-0.071	-0.0499
C	0.0021	0.0005
D	-0.0078	-0.0020
γ	-0.2044	-0.1104
β_1	1.5023	1.1102
β_2	0.0916	0.0170

The total energy is now constructed in the usual Kohn-Sham way[11]: the noninteracting kinetic energy is found by summing the occupied orbital energies E and subtracting off the interaction of each orbital with its effective potential V. To this we add the usual electrostatic energy

$$\int d^3r\, n(r)\left[-\frac{Z}{r}\right] + \frac{1}{2}\int d^3r \int d^3r'\, \frac{n(\vec{r})n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \tag{B5}$$

and the exchange-correlation energy (5).

Finally, we note that there are relativistic contributions of the form[33,34]

$$\Delta E_x^{\mathrm{LDA}}[n] = \int d^3r\, n(\vec{r})f(n(\vec{r}))\,, \tag{B6}$$

$$\Delta\mu_x^{\mathrm{LDA}}(n(\vec{r})) = \frac{\partial}{\partial n}[nf(n)]\,, \tag{B7}$$

to the exchange energy and potential in the local-density approximation, which become, respectively, in SIC:

$$\Delta E_x^{\mathrm{SIC}} = \Delta E_x^{\mathrm{LDA}}[n] - \sum_{\alpha\sigma} \Delta E_x^{\mathrm{LDA}}[n_{\alpha\sigma}] \tag{B8}$$

and

$$\Delta\mu_x^{\mathrm{LDA}}(n(\vec{r})) - \Delta\mu_x^{\mathrm{LDA}}(n_{\alpha\sigma}(\vec{r}))\,. \tag{B9}$$

Here

$$f(n)=\frac{9}{8}\left[\frac{3n}{\pi}\right]^{1/3}\left[\frac{\beta\eta-\ln\xi}{\beta^2}\right]^2, \qquad \text{(B10)}$$

where $\beta=n^{1/3}/44.3$, $\eta=(1+\beta^2)^{1/2}$, and $\xi=\beta+\eta$.

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*Present address: Solar Energy Research Institute, Golden, Colorado 80401.

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