Electron affinity of fluorine: A quantum Monte Carlo study

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Electron affinity of fluorine: A quantum Monte Carlo study[a]

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The total nonrelativistic energies of the fluorine atom and its negative ion are calculated using the fixed-node quantum Monte Carlo (QMC) method. Over 90% of the correlation energy is obtained for both the neutral and the anion. Subtracting these energies yields an electron affinity of 3.45 ± 0.11 eV, in excellent agreement with the recommended experimental value of 3.40 eV. The observed dependence of our Monte Carlo energies on the time step is discussed within the short-time QMC formalism. As in previous QMC studies in this series, only a single determinant, constructed with a small (double-zeta) basis set, multiplied by simple functions of electron–electron and electron–nuclear separation, is required as an importance function.

I. INTRODUCTION AND BACKGROUND

The accurate determination of electron affinities (EAs) remains a challenging theoretical task because the total energies of an atom or molecule and its anion must be computed to the same accuracy. The difference of these total energies is difficult to calculate using standard *ab initio* approaches because, at a given level of wave function and basis set expansion, the neutral and the anion are usually described to different levels of accuracy, and the appropriate level for each is not clear. This shortcoming of standard theoretical methods makes desirable an exploration of alternative theoretical techniques for obtaining EAs. In this paper a relatively new technique, quantum Monte Carlo (QMC) with fixed nodes, is employed to calculate the total energies of F and F⁻. Though the present calculations use relatively small basis sets and only single determinant trial functions, the energies obtained yield an EA for F in excellent agreement with experiment.

The history of EA calculations begins effectively with a few semiempirical estimates of the EA of F and other atoms in the late 1960's.[1,2] In those studies, correlation energies for atoms and positively charged ions were estimated by configuration interaction (CI) methods. Nonrelativistic "experimental" correlation energies[3] (also for the atoms and the positive ions) were combined with these CI energies to infer correlation energies for the negative ions. Electron affinities were thus deduced from experimental results and CI estimates of the correlation energies of atoms and *cations*.

Because it is desirable to compute physical quantities without reliance on experimental data, several *ab initio* studies of EAs were undertaken in the early 1970's.[4,5] To compute reliable *ab initio* EAs requires the accurate treatment of electron correlation. This is readily demonstrated by the poor quality of Hartree–Fock (HF) EAs.[6] Among the first-row atoms, for example, HF theory correctly predicts the *sign* of the EA for only two cases. Even for these systems the HF EAs are only 40% of the experimental values.

To incorporate correlation effects, Weiss[4] and Moser and Nesbet[5] employed the atomic Bethe–Goldstone method to calculate total energies for first-row atoms and ions. The technique relies on two assumptions: (a) that the total energy can be written

$$E = E_0 + \sum_n \epsilon_n + \sum_{mn} \epsilon_{mn} , \qquad (1)$$

where E_0 is the HF energy and ϵ_n and ϵ_{mn} are one- and two-particle correlation energies, respectively; and (b) that these correlations can be calculated independently using a superposition of configurations wave function. That is, the correlation energy of the mnth pair, ϵ_{mn}, is taken to be the energy lowering (relative to HF) upon including *only* double excitations of the mn pair in a CI expansion. The Moser–Nesbet and the Weiss EAs were found to be in good accord with experiment, having an error of only 2% for F.

Sasaki and Yoshimine[7] (SY), however, showed that summing one- and two-particle correlations, as implied in Eq. (1), would overestimate the EA of F by about 6% (0.20 eV) if a complete basis set were used. The SY study involved extended basis sets and large CI expansions in computing absolute energies of the first-row atoms and their singly charged anions. The basis sets contained up to i functions ($l = 6$), while the configuration list consisted of all single and double excitations from the lowest-energy configuration, as well as selected triples and quadruples. Though the SY total energies for F and F⁻ are the lowest obtained to date from variational calculations—having achieved over 95% of the correlation energy—the EA is nevertheless 0.28 eV (8%) less than the observed value. Thus SY's study again demonstrates the difficulty of determining the EA of F (and other atoms) by variational techniques.

Recently, several new theoretical estimates of the EA of F have been reported.[8–11] The techniques employed include many-body perturbation theory[8,9] as well as multiconfiguration self-consistent field plus CI methods.[10,11] These sophisticated treatments still result in errors of 4%–10%. Most recently, Møller–Plesset perturbation theory computations[12] have yielded an accurate EA of 3.47 eV, which is within 2% of experiment.

It is worth noting that the experimental determination of EAs is also difficult, with experimental values for the EA

of F ranging from 3.4–3.5 eV.[13-15] Presently, however, the recommended EA of F is 3.40 eV.[15] For a further discussion of the experimental work, see Ref. 10.

In the remainder of this paper we discuss the QMC approach to EA calculations. Section II briefly describes the QMC method used in this study, while Sec. III introduces the importance functions employed. Following this, Sec. IV presents and discusses the QMC total energies obtained for F and for F$^-$, and the resulting EA. Concluding remarks comprise the last section.

II. FIXED-NODE QUANTUM MONTE CARLO

Different variants of the basic QMC theme exist.[16,21,23,25-29] The diffusion QMC technique involves transforming the Schrödinger equation into a diffusion-like equation, and then solving the transformed problem using stochastic methods. The treatment we follow involves the fixed-node approximation[30] within the diffusion QMC approach. Chemical applications of QMC have most frequently used the current approach, and have involved calculations on a number of 2–10 electron systems.[16-20,24,28] The total energies obtained have been very accurate and, though statistical upper bounds due to the fixed-node approximation, have usually been lower than all previous variational results. We briefly outline the method below. For a full discussion of the theory and its implementation, see, e.g. Refs. 16 and 29.

The time-dependent electronic Schrödinger equation in imaginary time can be transformed into

$$\frac{\partial f}{\partial t} = D\nabla^2 f - D\nabla \cdot (F_Q f) + (E_T - E_L) f. \qquad (2)$$

Here

$$f(\mathbf{R},t) \equiv \Psi_I(\mathbf{R})\Phi(\mathbf{R},t) , \qquad (3a)$$

$$E_L(\mathbf{R}) \equiv H\Psi_I(\mathbf{R})/\Psi_I(\mathbf{R}) , \qquad (3b)$$

$$F_Q(\mathbf{R}) \equiv 2\nabla\Psi_I(\mathbf{R})/\Psi_I(\mathbf{R}) , \qquad (3c)$$

and

$$D\nabla \equiv \frac{\hbar^2}{2m_e} \sum_i \nabla_i . \qquad (3d)$$

The function $\Phi(\mathbf{R},t)$ is the imaginary-time wave function of the system at time t, while $\Psi_I(\mathbf{R})$ is an importance function (wave function) chosen to improve the efficiency of the technique. Note that Eq. (2) describes diffusion under the influence of an external force, F_Q, together with a rate or branching process whose rate "constant" is $[E_T - E_L(\mathbf{R})]$.

Knowledge of the Green's function, which is the solution of Eq. (2) with the boundary condition $G(\mathbf{R}\to\mathbf{R}',t=0) = \delta(\mathbf{R} - \mathbf{R}')$, is essential if one is to exactly carry out the "random walk," i.e., the diffusion, drifting, and branching implied by Eq. (2). For most systems, however, an analytic form of G is unknown. In the diffusion QMC approach this difficulty is surmounted by using an analytic approximation to G which is exact in the limit $t\to 0$ (except perhaps at the nuclei). As short times $t = \tau$, G may be interpreted as a product of the probability of moving from $\mathbf{R}$ to $\mathbf{R}'$ in time τ, and a weight representing the branching effect. Exact methods of sampling the Green's function also exist,[21-24] but often suffer from other disadvantages when

combined with the fixed-node approximation. For example, in the domain Green's function method[21,22] one must use small values of τ, which greatly reduces efficiency; in an approach[23] which overcomes this problem, a time-step bias is re-introduced due to undetected crossing of nodes.

As mentioned above, diffusion QMC is employed here; an approximate form, G_a, is used for the Green's function. As a result, in order to achieve an unbiased energy one must compute means at several time steps and extrapolate to $\tau = 0$. In previous work[16-20] the time-step dependence was found to be very weak, often being beneath the statistical noise, and extrapolation was unnecessary. Here we will see that this is not always the case.

To compute the energy of a state, one uses G_a to evolve an initial distribution $f(\mathbf{R},0)$—usually chosen to be $|\Psi_I(\mathbf{R})|^2$—to an asymptotic form. In practice the asymptotic distribution is obtainable after a short period of evolution, and is easily shown[16] to be proportional to

$$f_\infty(\mathbf{R}) = \Psi_I(\mathbf{R})\phi_0(\mathbf{R}) , \qquad (4)$$

where $\phi_0(\mathbf{R})$ is the *lowest-energy* eigenfunction which is not orthogonal to $\Psi_I(\mathbf{R})$. Once $f_\infty(\mathbf{R})$ is obtained, quantities such as the local energy $E_L(\mathbf{R})$ are sampled from this distribution. The average of the local energy E_L is a Monte Carlo estimator of ϵ_0, where ϵ_0 is defined by $H\phi_0 = \epsilon_0\phi_0$. By an estimator we mean that

$$\epsilon_0 = \lim_{N\to\infty} \frac{1}{N} \sum_{i=1}^{N} E_L(\mathbf{R}_i) . \qquad (5)$$

Since electrons are fermions, it is necessary in chemical applications to compute properties for a Fermi state. Because the Schrödinger equation usually has one or more Bose-state solutions—i.e., solutions symmetric with respect to particle interchange—which are lower in energy than the Fermi ground state, the QMC method as described above will generally converge to a physically meaningless state. One method of forcing antisymmetry is to impose fixed exchange nodes on the solution ϕ_0. One can accomplish this by letting the nodes of ϕ_0 be the nodes of a trial wave function Ψ_T. This is equivalent to adding a potential which is infinite where $\Psi_T = 0$. Another way of viewing this is that the Schrödinger equation (with only the original Coulomb potential) is solved with the nodes of Ψ_T as additional boundary conditions. These boundary conditions are usually approximate, since the nodal structure of most chemical states is unknown. Thus a "fixed-node" error is introduced.[31] This error is, however, variationally bounded.[16,29] In previous work,[16-20] generally 95% or more of the correlation energy was obtained, implying that the fixed-node error is quite small for simple (e.g., one determinant) choices of Ψ_T. For simplicity we choose $\Psi_T = \Psi_I$.

III. IMPORTANCE FUNCTIONS

A good QMC importance function, Ψ_I, should be easy to evaluate, and yet mimic the desired eigenfunction. Ease of evaluation is useful in limiting computational effort, because quantities such as F_Q and E_L [cf. Eq. (3)] can be computed quickly. On the other hand, it is important to mimic the true eigenfunction because in the limit $\Psi_I \to \phi_0$ the variance of E_L

vanishes, i.e., $H \phi_0/\phi_0 = \epsilon_0$ a constant; additionally, as the nodal structure becomes exact so does the eigenvalue ϵ_0. Unfortunately, ease of evaluation of Ψ_I generally works against accuracy and precision. Thus one is forced to compromise in the importance functions one uses.

Earlier studies[16–19] used small basis set, single determinant importance functions. In each of these works, electron correlation was introduced explicitly by multiplying the determinant by an electron–electron correlation function of the Jastrow form [cf. Eq. (7) below]. An electron–nuclear Jastrow function [cf. Eq. (8) below] was also found to be necessary to offset the global expansion of the electron distribution caused by the electron–electron Jastrow factor. These factors reduced the statistical error at small computational cost. Importance functions of this type are also used in this study and have the form

$$\Psi_I = \det|\psi_k^\alpha|\det|\psi_k^\beta|J_1(r_{ij})J_2(r_{i\gamma}) . \tag{6}$$

The product of determinants is derived from a standard Slater determinant by assigning spins (α or β) to each of the electrons.[32] The ψ_k are molecular orbitals (MOs) whose linear coefficients are obtained from self-consistent field (SCF) calculations;[33] basis sets used are displayed in Table I. The Jastrow factors are

$$J_1(r_{ij}) = \exp\left(\sum_{i<j} \frac{a_1 r_{ij} + a_2 r_{ij}^2}{1 + b_1 r_{ij} + b_2 r_{ij}^2}\right) \tag{7}$$

and

$$J_2(r_{i\gamma}) = \exp\left(-\sum_{i\gamma} \frac{\lambda r_{i\gamma}}{1 + v r_{i\gamma}}\right). \tag{8}$$

The parameter a_1 is chosen to satisfy the cusp condition for electrons of unlike spin;[34] the remaining parameters may be variationally optimized. The coordinates r_{ij} represent electron–electron separations while $r_{i\gamma}$ represent electron–nuclear separations. Note that the Jastrow factors are positive definite, and therefore do not affect the nodes.

TABLE I. Parameters used in Ψ_I. The exponents and linear coefficients for F are taken from Ref. 33(a); the Jastrow parameters are hand optimized. For F$^-$, linear coefficients were obtained using HONDO [Ref. 36(b)], while exponents and Jastrow parameters were hand optimized. Jastrow parameters are given in atomic units.

		F	F$^-$
Exponents[a]	1s	10.424 50	10.200
	1s'	7.665 85	7.250
	2s	3.135 78	3.100
	2s'	1.944 56	1.700
	2p	4.183 89	4.125
	2p'	1.856 02	1.650
Jastrow parameters[b]	a_1	0.50	0.5000
	a_2	0.00	2.8750
	b_1	3.00	11.5000
	b_2	0.00	33.0625
	λ	0.10	0.1000
	v	0.10	0.2000

[a] Parameters of one-electron Slater basis set.
[b] See Eqs. (7) and (8).

IV. RESULTS AND DISCUSSION

In Table II our QMC results are compared with previous studies. The QMC total energies are quite good, achieving over 90% of the correlation energy for both F and F$^-$. These energies are lower than those of previous variational calculations, with the sole exception of those of SY.[7] It should be pointed out, however, that it is quite difficult to perform such large basis set, extended CI calculations, as done in Ref. 7, on most chemical systems. Moreover, the QMC electron affinity gives better agreement with experiment[35] than that of SY, as well as giving better agreement than all other variational calculations. Moreover, the present QMC EA is also as good as or better than nonvariationally obtained EAs.

Our QMC energies for several time steps, τ, are presented in Table III, and shown graphically in Fig. 1. In the figure one sees that the fixed-node energies of F and F$^-$ increase with decreasing τ. Furthermore, the data strongly suggests that the energy is linear in τ for small τ. As can be seen in Fig. 1, it appears that the F$^-$ energy has begun to deviate from linearity by $\tau = 0.005$ hartree^{-1}, while the F energy remains linear in this region. In other words, the observed linear domain is smaller for F$^-$ than for F.

The variation of the fixed-node energy with τ which we obtain is the result of two effects. First, we use an approximate Green's function, which becomes exact only in the limit $\tau \to 0$. Second, we neglect the probability that a particular walker crosses and then recrosses a node during a move. In general, this probability cannot be calculated exactly; however, not incorporating this probability into the random walk, or incorporating it only approximately, gives rise to a "cross–recross" bias. The cross–recross effect increases with increasing time step. This is because a larger time step allows a walker to wander further during a move, making it more likely that it actually crossed and recrossed a node. This effect would appear to lower the energy, since it results in a partial removal of the nodal constraints, causing a "Bose perturbation" on the distribution f_∞.

The bias caused by the approximate form of the Green's function is harder to assess. For the ground state of H_2, where no cross–recross bias exists (there are no nodes), the QMC energy decreases as the time step decreases.[16] On the other hand, for the ground state of H, we have found the energy to increase as the time step decreases. Furthermore, the amount of bias is dependent on the importance function used. For systems in which there is both a Green's function bias and a cross–recross bias, it is hard to separate the two effects.

At the short time steps needed to avoid a significant bias, the efficiency of QMC is degraded because the steps of the random walk are highly correlated. Independent sampling is only observed through blocking of data into segments of large enough time. The smaller τ is, the longer it takes computationally to achieve an "independent" block. As an example of the computing required, at $\tau = 0.005$ hartree^{-1}, roughly 4 h of Cray time were needed to calculate the energy for F, and similarly for F$^-$, to the accuracy shown in Table II. For the time steps used in these calculations, halving τ doubles the computer time needed to achieve a given statisti-

TABLE II. Comparison of theoretical and experimental total energies of F and F$^-$, and electron affinities of F. Total energies are in hartrees and EAs in electron volts. The empirical energies are estimates of the total nonrelativistic energy, and are obtained by subtracting relativistic corrections from experimental energies. Uncertainties are indicated in parentheses.

		Energy (hartree)		
	Method	F	F$^-$	EA (eV)
Ab initio non variational	Atomic Bethe–Goldstone	− 99.7131[a]	− 99.8411[a]	3.47[a] 3.37[b]
	Perturbation theory	− 99.7299[c] − 99.6750[d]	− 99.8595[c] − 99.8025[d]	3.53[c] 3.47[d]
Ab initio variational	HF[e]	− 99.4093	− 99.4594	1.36
	CI[f]	− 99.7166	− 99.8312	3.12
	MCSCF + CI	− 99.6202[g] − 99.62350[h]	− 99.7369[g] − 99.73722[h]	3.18[g] 3.09[h]
	QMC[i]	− 99.7005(21)	− 99.8273(34)	3.45(11)
	Empirical	− 99.7313[j]	− 99.8574(30)[k]	3.43(8)[l]
	Experimental	− 99.8059[m]	⋯	3.399(3)[n]

[a] Reference 4.
[b] Reference 5.
[c] Reference 8.
[d] Reference 12.
[e] Reference 6.
[f] Reference 7.
[g] Reference 10.
[h] Reference 11.
[i] This work.
[j] From experimental results corrected for relativistic effects in Ref. 3. Reference 7 corrects an error in the sign of the Lamb shift, resulting in the energy given here.
[k] Reference 36.
[l] This number is the difference of the empirical values for F and F$^-$. See also Ref. 35.
[m] Reference 37.
[n] Recommended experimental value of Ref. 15.

cal accuracy. A reliable extrapolation to $\tau = 0$ requires the use of time steps sufficiently small that the asymptotic behavior of the energy is observed. Therefore, it is desirable to reduce the time-step bias both through a more accurate Green's function and by properly handling the cross–recross probability. Work in these directions is currently being pursued.

The main difficulty encountered in variational calculations of EAs is that of describing the atom and the anion to the same accuracy. Generally, the atom, being easier to describe than the anion, is treated more accurately at the same level of theory. This leads to an underestimation of the EA.

Even for a large basis set, large CI calculation, such as that of SY, this effect persists. For example, SY underestimate the EA of F by 0.28 eV. On the other hand, using relatively simple importance functions, i.e., double-zeta-basis-set single determinants, QMC appears to treat F and F$^-$ to virtual-

TABLE III. Fixed-node energies of F and F$^-$. The statistical uncertainties (one standard deviation) are shown in parentheses. The total energies for F and F$^-$ are obtained from a linear extrapolation to $\tau = 0$ of the energies at the three smallest time steps.

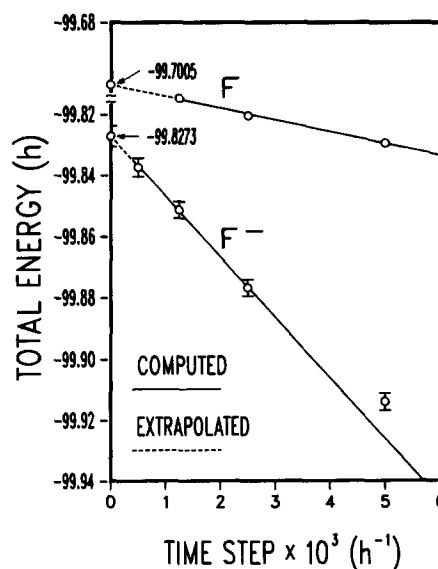|	Energy (hartree)	
Time step (hartree^{-1})	F	F$^-$
0.005 00	− 99.7196(17)	− 99.9141(28)
0.002 50	− 99.7106(20)	− 99.8769(28)
0.001 25	− 99.7050(17)	− 99.8515(27)
0.000 50	⋯	− 99.8375(31)
0.0 (extrapolation)	− 99.7005(21)	− 99.8273(34)

FIG. 1. Fixed-node energy vs time step. For F, the error bars are contained within the points.

ly the same accuracy (i.e., the EA is in error by 0.05 ± 0.11 eV). Apparently, the quality of the *nodal structures* obtained in the SCF procedure does not vary significantly from F to F^-, and so the fixed-node error in the energy is about the same for the two systems.

V. CONCLUDING REMARKS

In this study we have calculated the energies of F and F^- using a fixed-node QMC approach. We have obtained an EA for F of 3.45 ± 0.11 eV which is in excellent agreement with the recommended experimental value of 3.40 eV. The QMC energies show a significant bias for the finite time steps used. Removing this bias through extrapolation is found to significantly reduce the efficiency of the calculation and thus lower the statistical precision obtainable for a given amount of computer time. Therefore, alternative methods of removing this bias are recommended for future studies on systems with $Z \gtrsim 10$. Nevertheless, the absolute energies obtained here are quite good, leading to one of the best theoretical determinations of the EA of the fluorine atom to date.

ACKNOWLEDGMENT

[1] İ. Öksüz and O. Sinanoğlu, Phys. Rev. **181**, 54 (1969).

[2] H. F. Schaefer III, R. A. Klemm, and F. E. Harris, J. Chem. Phys. **51**, 4643 (1969).

[3] A. Veillard and E. Clementi, J. Chem. Phys. **49**, 2415 (1968).

[4] A. W. Weiss, Phys. Rev. A **3**, 126 (1971).

[5] C. M. Moser and R. K. Nesbet, Phys. Rev. A **4**, 1336 (1971); **6**, 1710 (1972).

[6] S. Fraga, J. Karwowski, and K. M. S. Saxena, *Handbook of Atomic Data* (Elsevier, Amsterdam, 1976).

[7] F. Sasaki and M. Yoshimine, Phys. Rev. A **9**, 17, 26 (1974).

[8] K. Jankowski, P. Malinowski, and M. Polasik, Phys. Rev. A **22**, 51 (1980).

[9] S. A. Kucharski, Y. S. Lee, G. D. Purvis III, and R. J. Bartlett, Phys. Rev. A **29**, 1619 (1984).

[10] B. H. Botch and T. H. Dunning, Jr., J. Chem. Phys. **76**, 6046 (1982), and references therein.

[11] B. O. Roos, A. J. Sadlej, and P. E. M. Siegbahn, Phys. Rev. A **26**, 1192 (1982).

[12] K. Raghavachari, J. Chem. Phys. **82**, 4142 (1985).

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

[14] R. S. Berry and C. W. Reiman, J. Chem. Phys. **38**, 1540 (1963).

[15] H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data **4**, 539 (1975).

[16] P. J. Reynolds, D. M. Ceperley, B. J. Alder, and W. A. Lester, Jr., J. Chem. Phys. **77**, 5593 (1982).

[17] P. J. Reynolds, R. N. Barnett, and W. A. Lester, Jr., Int. J. Quantum Chem. Symp. **18**, 709 (1984).

[18] P. J. Reynolds, M. Dupuis, and W. A. Lester, Jr., J. Chem. Phys. **82**, 1983 (1985).

[19] R. N. Barnett, P. J. Reynolds, and W. A. Lester, Jr., J. Chem. Phys. **82**, 2700 (1985).

[20] J. B. Anderson, J. Chem. Phys. **63**, 1499 (1975); **65**, 4121 (1976); **73**, 3897 (1980).

[21] M. H. Kalos, D. Levesque, and L. Verlet, Phys. Rev. A **9**, 2178 (1974).

[22] D. M. Ceperley and M. H. Kalos, in *Monte Carlo Methods in Statistical Physics*, edited by K. Binder (Springer, Berlin, 1979), pp. 145–197.

[23] D. M. Ceperley, J. Comput. Phys. **51**, 404 (1983).

[24] D. M. Ceperley and B. J. Alder, J. Chem. Phys. **81**, 5833 (1984).

[25] M. H. Kalos, Phys. Rev. **128**, 1791 (1962).

[26] W. L. McMillan, Phys. Rev. **138A**, 442 (1965).

[27] D. M. Ceperley, G. V. Chester, and M. H. Kalos, Phys. Rev. B **16**, 3081 (1977).

[28] J. W. Moskowitz, K. E. Schmidt, M. A. Lee, and M. H. Kalos, J. Chem. Phys. **77**, 349 (1982).

[29] D. M. Ceperley, in *Recent Progress in Many-Body Theories*, edited by J. G. Zabolitzky, M. de Llano, M. Fortes, and J. W. Clark (Springer, Berlin, 1981), pp. 262–269.

[30] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[31] The relaxation of the fixed-node constraint is described in Refs. 24 and 30.

[32] Since the Hamiltonian is spin independent, the energy is not affected by these assignments.

[33] (a) For F, see E. Clementi and C. Roetti, At. Data Nucl. Data Tables **14**, 177 (1974); (b) For F^- the computer code HONDO was used. [NRCC Software Catalog 1, 60 (1980), LBL-10811, UC-4. Available from the National Technical Information Service, U. S. Department of Commerce, 5285 Port Royal Road, Springfield, Virginia 22161; price code: A05.]

[34] For electrons of like spin the value of a_1 which satisfies the electron–electron cusp condition is actually half the value of a_1 for electrons of unlike spin (see Ref. 16). Since the Fermi hole, inherent in the determinantal form of Ψ_I, tends to keep electrons of like spin apart, it is probably less important to maintain the cusp condition for like spins than for unlike spins.

[35] As can be seen in Table II, nonrelativistic energies can be used to obtain an accurate EA for F. This is because relativistic corrections to the energies of F and F^- are practically equal. See, for example, Ref. 36.

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

[37] R. C. Kelly, *Atomic and Ionic Spectrum Lines Below 2000 Å*, Oak Ridge National Laboratory-5922 (1982). [Available from National Technical Information Service, U. S. Department of Commerce, 5285 Port Royal Road, Springfield, Virginia 22161; price code: A19.]