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Commentationes

Thomas-Fermi-Dirac Calculations for Molecules

II. One-Electron Energies for F_2

JERRY GOODISMAN*

Department of Chemistry, Syracuse University, Syracuse, N.Y. 13210, USA

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The electrostatic potential derived from a solution to the molecular Thomas-Fermi-Dirac equation for F_2 is combined with the exchange potential and modified to give the correct behavior far from the nuclei. One-electron energy levels in this potential are calculated and are in qualitative agreement with SCF orbital energies. Similar computations are carried through for F and Ar, which correspond to the separated and united atoms for F_2. To compensate for errors in the potential, we subtract from molecular orbital energies the difference of TFD and SCF orbital energies for the separated atoms. Now all the orbital energies are correct to a few electron volts.

Das elektrostatische Potential, das sich für F_2 aus der Thomas-Fermi-Dirac Theorie ergibt, wird mit dem Austauschpotential kombiniert und so modifiziert, daß sich das richtige Verhalten in Kernnähe ergibt. Die berechneten Einelektronenenergien sind in qualitativer Übereinstimmung mit SCF-Werten. Analoge Rechnungen für F und Ar werden ausgeführt und als Grenzfälle für Korrekturen verwendet. Dann ergeben sich alle Orbitalenergien bis auf wenige eV richtig.

1. Introduction

The Thomas-Fermi-Dirac theory [1] gives a relation between electron density and electrostatic potential which, coupled with the Poisson equation, yields a differential equation from which either of these two quantities may be determined. This provides a simple route to approximate electron densities for many-electron systems, such as atoms and molecules. However, it appears [2] that the densities are not sufficiently accurate for many molecular properties, whose values are differences between nuclear and electronic contributions.

One may also consider using the results given by the theory for the potential seen by an electron at any point within the system. One can calculate the energy levels and wavefunctions of a single electron in this potential, and build up the atomic or molecular wavefunction from these. The energies are first approximations to the one-electron eigenvalues of the Hartree-Fock equations. By Koopman's Theorem, these approximate to ionization potentials, while differences between them may be related to the energies of electronic transitions [3]. For molecules, the variation of these energies with nuclear configuration is used to predict equilibrium nuclear positions and potential constants [4, 5].

In this article, we report the one-electron eigenvalues for diatomic fluorine near its equilibrium internuclear distance, using a potential derived from the solution to the Thomas-Fermi-Dirac equation. A number of calculations of this kind have been made in the past for atoms [1], but to our knowledge there is

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only one for a molecule: Recknagel [6] in 1934, considered the term values of N_2 and N_2^+ using the Thomas-Fermi potential for the neutral homonuclear diatomic system of 13 electrons plus the Coulombic potential of two nuclei of charge $\frac{1}{2}e$. The energies of the lowest terms of N_2^+ and some excited terms of N_2 relative to ground state N_2 were calculated from differences of orbital energies (correcting for the change of equilibrium internuclear distance in the first case) and proved accurate to 1–2 eV.

The most complete tabulation of atomic results, for both the T–F and TFD fields, was given by Latter [7]. Unfortunately, he used an approximation to the TFD potential which means his eigenvalues are significantly changed. More recent workers [8] also used approximate potentials. An exception is Yonei [9], who treated K and Cs with a potential derived from a TFD calculation in which a Weizsäcker correction [1] (x 0.2) was used. Results were quite good for energies, and fair for calculated oscillator strengths. For the valence electron, a complicated modification of the exchange potential improved the results.

The computations are described in the next section. The results are discussed in Sect. 3. In Sect. 4, we investigate the use of atomic results to correct the molecular eigenenergies for the defects of the potential. The calculated atomic energy levels in the Thomas-Fermi-Dirac potential by Latter could not be used because of the approximations he introduced, and we have had to recalculate the results for atomic systems. Sect. 5 summarizes our conclusions.

2. Method of Calculation

The approximate solution of the Thomas-Fermi-Dirac equation for a homonuclear diatomic molecule, obtained by a relaxation method discussed and used by Sheldon [10], has been used [2] to generate approximate electron densities for several homonuclear diatomic systems. In terms of the function u used in those computations, the potential at some point in space r is given by:

$$V = u^2(R\xi\pi^2)^{-1} - (32\pi^2)^{-1}. \tag{1}$$

Here, R is the internuclear distance and $\xi^{-1} = r_A^{-1} + r_B^{-1}$, r_A and r_B being the distances to nuclei A and B. Atomic units are used ($e = \hbar = m = 1$), with the charge on the electron taken as -1.

It has been shown for many quantum mechanical calculations [11] that the exchange energy may be represented as the interaction of the electron density ϱ with an *exchange potential* $(3/2)(3/\pi)^{\frac{1}{3}}\varrho^{\frac{1}{3}}$. This is added to V. Expressing ϱ in terms of the function u gives for the total potential

$$V' = V + (3/4\pi^2)\left[1 + u(\tfrac{1}{2}\xi R)^{-\frac{1}{2}}\right]. \tag{2}$$

The exchange potential is set equal to zero outside the boundary of the system, where the electron density drops discontinuously to zero. Since V' does not approach a Coulombic potential as one goes far away from the nuclei, as it should, Latter suggested for atoms [7] that V' be used whenever it is greater than r^{-1} and that V' be replaced by r^{-1} when it drops below this. For the diatomic molecule, we maintain the expected shape of the problem by replacing V' by $\frac{1}{2}\xi^{-1}$ at all points in space where it goes below this quantity. It turns out that replacing $\frac{1}{2}\xi^{-1}$ by r_0^{-1}, r_0 being the distance from the molecular midpoint, changes our results little.

The equation which gives the eigenvalues is

$$-\tfrac{1}{2}\nabla^2\psi - V'\psi = \varepsilon\psi \tag{3}$$

and is treated by linear variation. The matrix elements are evaluated numerically, using crossed Gaussian quadrature formulas, over the two-dimensional grid of points used to determine u, extended to larger and smaller distances from the nuclei. Outside the boundary of the molecule, the potential is simply Coulombic, $V = \frac{1}{2}\xi^{-1}$. Close to the nuclei, where the molecular potential for F_2 is essentially that of the F atom, we use the atomic function ψ as a series in $r^{\frac{1}{2}}$ to compute V and add the corresponding exchange potential. The coordinates used [2] are ξ and η; if ξ is thought of as giving the distance from the nuclei and hence replacing r for a one-center system, η may be considered as giving angular position. Errors in the resulting eigenvalues could be due to numerical inaccuracies or to insufficiently flexible basis sets. The latter will make all the eigenvalues too high, according to the linear variational principle. The former probably would make them too low, since the use of sums for integrals is a removal of some restrictions on the trial function. The estimation of the overall error is discussed below.

It was thought originally that a reasonable and convenient set of basis functions would be

$$X_i = \xi^{j_i}\eta^{k_i}e^{-\alpha\xi} \tag{4}$$

(j and k positive integers, α a parameter to be determined) for σ_g orbitals, with multiplication by suitable factors of $e^{i\varphi}$, x, and r (distances from the midplane and from the symmetry axis) for orbitals of other symmetries. This turns out not to be so, because of the properties of the coordinate system, which can only be characterized as pathological. Sheldon [10] shows that the Laplacian of a φ-independent function f at the molecular midpoint ($\xi = \frac{1}{2}, \eta = 0$) is given by

$$\nabla^2 f = (\partial f/\partial\xi)_+ - (\partial f/\partial\xi)_-$$

where $(\partial f/\partial\xi)_\pm$ is the derivative for $\xi = \frac{1}{2} \pm \varepsilon, \varepsilon \to 0$. Thus any function which is continuous in ξ at this point has a zero kinetic energy here – an unnecessary restriction on the trial function. We decided to use the usual basis functions for the homonuclear diatomic problem.

For σ_g orbitals,

$$X_i = \lambda^{m_i}\mu^{n_i}e^{-\alpha\lambda} \tag{5}$$

with m_i an integer, n_i an even integer, and α to be determined. Here, λ and μ are the confocal ellipsoidal coordinates,

$$\lambda = (r_A + r_B)/R;\ \mu = (r_A - r_B)/R\,, \tag{6}$$

where r_A and r_B are distances to the nuclei A and B and R is the internuclear distance. For σ_u orbitals, (5) was used with n_i odd. For π_g orbitals, we used

$$X_i = \lambda^{m_i}\mu^{n_i}e^{-\alpha\lambda}e^{im\varphi}[(\lambda^2-1)(1-\mu^2)]^{\frac{1}{2}} \tag{7}$$

Table 1. Eigenvalues in a two-center coulombic potential

Symmetry species	Our calculation α_{best}	$-\varepsilon$(a.u.)	Exact[a] $-\varepsilon$(a.u.)
σ_g	0.92	0.9664	0.9619
σ_g	0.91	0.3327	0.3308
σ_g	0.95	0.2493	0.2494
σ_g	0.77	0.1674	0.1670
σ_u	1.22	0.7020	0.6966
σ_u	0.74	0.2551	0.2549
σ_u	0.60	0.1384	0.1364
σ_u	0.60	0.1330	0.1280
π_u	1.23	0.3994	0.3993
π_u	0.77	0.1943	—
π_g	0.91	0.2299	0.2289
π_g	0.79	0.1335	—

[a] Bates, D. R., Ledsham, K., Stewart, A. L.: Philos. Trans. Roy. Soc. (London) A**246**, 215 (1953).

with n_i odd; for π_u orbitals, we used (7) with n_i even. Twelve basis functions were used initially in all the calculations reported here. In most cases, near linear dependencies reduced this number to nine or ten. For each eigenvalue, a series of calculations were made with different values of α until the energy as a function of α passed through a minimum. Three values were fitted to a parabola to determine the best α. All calculations were programmed in Fortran for the IBM 360.

In order to assess the accuracy of the calculation, we evaluated eigenvalues in the coulombic potential

$$V=\xi^{-1}=r_A^{-1}+r_B^{-1}$$

at an internuclear distance of 2.68 a_0. The energies of many of the states of this system, the H_2^+ molecular ion, are known from exact calculations. In Table 1 we give our results and compare with the exact values. It may be seen that our energies are correct to better than 0.01 a.u.

3. Results for F_2

For F_2 at an internuclear distance of 2.68 a_0, the same calculations were carried through, with results given in Table 2. We have also given the orbital energies from a matrix Hartree-Fock calculation. Atomic units (1 a.u. = 27.21 eV) are used for energies throughout. At the outset, we note that there is qualitative agreement for all the orbital energies.

The inner-shell energies are 1 a.u. too high, due to the fact that the Thomas-Fermi-Dirac model gives too high an electron density near the nuclei (at the nucleus the density is actually predicted to be infinite) so that V does not rise as rapidly as it should as one approaches a nucleus (the exchange potential is of minor importance here). For the energies of about -1 a.u., which include the highest filled levels, our results are several tenths of an a.u. too low. For the energies between these groups, the agreement with SCF is good.

Table 2. Orbital energies for F_2

Orbital	α_{best}	ε(a.u.)	ε(a.u.) from SCF[a]
$1\sigma_g$	11.9	−25.33	−26.423
$2\sigma_g$	5.4	− 1.828	− 1.757
$3\sigma_g$	4.2	− 1.091	− 0.746
$1\sigma_u$	11.2	−25.36	−26.422
$2\sigma_u$	5.4	− 1.573	− 1.495
$3\sigma_u$	4.4	− 0.791	—
$1\pi_u$	5.2	− 1.083	− 0.805
$1\pi_g$	5.3	− 0.943	− 0.663

[a] Wahl, A.C.: J. chem. Physics **41**, 2600 (1964).

The order of the energy levels,

$$1\sigma_g = 1\sigma_u < 2\sigma_g < 2\sigma_u < 3\sigma_g < 1\pi_u < 1\pi_g < 3\sigma_u$$

is almost correct; $1\pi_u$ should actually be slightly below $3\sigma_g$. The difference of energies for $1\sigma_g$ and $1\sigma_u$ (the former should actually lie slightly lower) we take as an indication of the maximum numerical error in our calculation. These wavefunctions vary more rapidly in space than those for H_2^+. The experimental ionization potential is 0.599 a.u., which is in much better agreement with the SCF orbital energy for the highest occupied orbital (0.663 a.u.) than that from the TFD potential (0.943 a.u.). On the other hand, the error in all the higher orbital energies is roughly the same, so differences in these quantities, which may be related to spectra, are close to SCF values:

$$\varepsilon_{1\pi_g} - \varepsilon_{1\pi_u} = 0.14 \text{ a.u. (TFD)}, 0.14 \text{ a.u. (SCF)}$$
$$\varepsilon_{1\pi_u} - \varepsilon_{3\sigma_g} = 0.01 \text{ a.u. (TFD)}, -0.05 \text{ a.u. (SCF)}$$
$$\varepsilon_{1\pi_u} - \varepsilon_{2\sigma_u} = 0.49 \text{ a.u. (TFD)}, 0.69 \text{ a.u. (SCF)}$$

and so on.

The predicted electron affinity is the negative of the energy of the lowest unoccupied orbital, $-\varepsilon_{3\sigma_u} = 0.79$ a.u., and is undoubtedly at least three tenths of an atomic unit too high, but the energy of the lowest energy one-electron transition, $\varepsilon_{3\sigma_u} - \varepsilon_{1\pi_g} = 0.15$ a.u., should be much closer to the correct result. [Actually (see below) the errors in σ and π orbitals probably do not cancel as well as those between two σ orbitals or two π orbitals.] The experimental value for F_2 is not available, but, if we extrapolate results for I_2, Br_2, and Cl_2 from Herzberg, we may estimate a frequency of 20×10^3 cm^{-1} which corresponds to 0.09 a.u.

While a log-log plot of TFD orbital energies vs. SCF orbital energies doesn't look bad, it must be admitted that agreement is not good enough to be considered quantitative. The poblem now becomes correction of the defects in the potential which led to the inaccuracies. The problem close to the nucleus seems relatively easy to correct [12], but the incorrect behavior of the higher energies seems less so. It may be, however, that the problems with the potential are common to both atoms and molecules. For atoms, SCF calculations are readily available, while TFD calculations are easily performed. For large molecules, only the latter may be possible. If the molecular orbitals can be correlated with atomic orbitals, corrections derived from the atomic work can be applied to the molecular energies. Such correlations are of course part of every quantum chemist's education. As is shown below, this leads to a great improvement in predicted orbital energies.

4. Atomic Calculations

Latter [7] gives an extensive tabulation of "Atomic Energy Levels for the Thomas-Fermi and Thomas-Fermi-Dirac Potential". However, he replaced the TFD potential, which must be calculated separately for each atom, by an approximate universal potential. Its deviation from the correct potential, it is stated, is less than five per cent for $Z > 5$. This is too large for our purposes. As we will see below, the changes in orbital energies due to this approximation are tenths of atomic units. It was thus necessary to compute energies for the true TFD potential for several atoms.

The differential equation for the radial part of an atomic wavefunction of orbital angular momentum l is

$$\frac{d^2\psi}{dr^2} + \left[\frac{2m\varepsilon}{\hbar^2} - \frac{2mV(r)}{\hbar^2} + \frac{l(l+1)}{r^2}\right]\psi = 0 \tag{8}$$

where ψ is the radial wavefunction multiplied by r. Using the fact that $\psi(0)=0$, we may substitute for (8) the integral equation

$$\psi(r) = r\psi'(0) - \int_0^r (r-r')\left[\frac{2m\varepsilon}{\hbar^2} - \frac{2m}{\hbar^2}V(r') + \frac{l(l+1)}{r'^2}\right]\psi(r')\,dr'\,. \tag{9}$$

Since ψ goes as r^{l+1} as r approaches 0, $\psi'(0)$ is 0 except for s states. The overall normalization of ψ is irrelevant for our purposes. As did Latter, we solve (9) as a difference equation, using equal spacing in $r^{\frac{1}{2}}$. We evaluate all integrals using a Newton-Cotes five-point rule. The orbital energy ε is determined, generally to 0.01 a.u., by integrating outward from $r=0$ for successive trial values of ε until we obtain one too high and one too low, as judged by following the behavior of the functions for large r. The computations were carried out using the APL system of the 360 computer.

We first verified the accuracy of our procedure and choice of spacing of points by calculating energies for the F atom in Latter's approximate potential. Latter used different integration formulas in his work. Then we solved the TFD equation for this atom and determined energy levels in the correct potential (the TFD potential corrected for exchange and proper asymptotic behavior as in the previous section). Results are given in Table 3. It is seen that our energies agree with those given by Latter for his potential.

It is also seen that there are substantial differences between the energies in the two potentials. For the 1s, the TFD result is 1 a.u. closer to the SCF result than Latter's; for the 2s and 2p, there is a difference of 0.1 a.u. in the other direction. It may also be interesting to note that Herman and Skillman [13], performing SCF calculations with the exchange term replaced by a local potential proportional to $\varrho^{\frac{1}{3}}$, obtained -25.27, -1.318 and -0.625 a.u. for the orbital energies.

Table 3. One-electron energies for fluorine atoms

Orbital	Latter[a]	Energy (a. u.) Latter pot.[b]	TFD pot.	SCF[c]
$1s$	-24.18[d]	-24.25	-25.38	-26.383
$2s$	-1.541	-1.55	-1.65	-1.573
$2p$	-0.858	-0.857	-0.96	-0.730

[a] Latter, R.: Physic. Rev. **99**, 510 (1955).

[b] Calculated with our programs using Latter's approximate potential.

[c] Clementi, E., Roothaan, C. C. J., Yoshimine, M.: Physic. Rev. **127**, 1618 (1962).

[d] Not given by Latter; interpolated from his Table using $-\varepsilon = kZ^a$.

Table 4. One-electron energies for argon atom (a. u.)

Orbital	ε, TFD pot.	ε, SCF pot.[a]
$2p$	-9.31	-9.58
$3s$	-1.08	-1.28
$3p$	-0.62	-0.59
$3d$	-0.061	—

[a] Czyzak, S. J.: Astrophysic. J. Supp. **7**, 53 (1962).

The TFD results are thus about as good (in the sense of approximating the SCF results) as these. In addition to the F atom, which represents the separated atoms for the F_2 molecule, we also want to consider the atom formed by F_2 when the internuclear distance approaches zero (united atom), Argon. Some energy levels calculated in the TFD potential for this atom are given in Table 4, and compared with SCF results.

The correlations of the molecular orbitals with orbitals of the united atom and separated atoms are easily obtained and are given in many sources [14]. It must be decided, for each orbital, whether the united atom or separated atom limit is more relevant. For the inner shell orbitals $1\sigma_g$ and $1\sigma_u$, there is little problem. When R is near the equilibrium internuclear distance these are essentially unaffected by the binding process. This is shown by comparing orbital energies for the molecule and the atoms, from the SCF or TFD calculations. The orbitals are $1s_A \pm 1s_B$, A and B denoting the two atoms, and the lack of substantial overlap between the atomic orbitals makes $\varepsilon_{1\sigma_g}$ and $\varepsilon_{1\sigma_u}$ close to equal. Of course, if the TFD results of Table 1 are corrected by addition of -1.00 a.u., the difference between SCF and TFD energies for the F $1s$ orbitals, we obtain approximately correct energies for the $1\sigma_g$ and $1\sigma_u$ orbitals: $\varepsilon_{1\sigma_g} = \varepsilon_{1\sigma_u} = -26.35$. We have used the average. The last figure may be in error by several units, as indicated by $\varepsilon_{1\sigma_u}$ being 0.03 a.u. *lower* than $\varepsilon_{1\sigma_g}$ in the TFD results.

The remaining molecular orbitals correlate with the $2s$ and $2p$ orbitals of the separated atoms, and with $2s$, $2p$, $3s$, $3p$, $3d$ and $4s$ of the united atom. In general, one expects that the orbitals of lower energy, which are less diffuse, are more closely related to the separated atom limit, and the higher energy orbitals closer to the united atom. The orbital energies provide some guidance here. Thus, $2\sigma_g$ correlates

Table 5. Corrected orbital energies

Orbital	AO used for comparison	Corrected ε(a. u.)
$1\sigma_g$	F 1*s*	-26.36
$2\sigma_g$	F 2*s*	$-\ 1.75$
$3\sigma_g$	F 2*p*, Ar 3*s*	$-\ 0.86, -1.29$
$1\sigma_u$	F 1*s*	-26.35
$2\sigma_u$	F 2*s*, Ar 3*p*	$-\ 1.49, -1.54$
$3\sigma_u$	F 2*p*	$-\ 0.56$
$1\pi_u$	F 2*p*	$-\ 0.85$
$1\pi_g$	F 2*p*	$-\ 0.71$

Table 6. Ionization potentials for F_2 (eV)

State	Orbital energies			Experimental[a]
	This work, uncorrected	This work, corrected	Hartree-Fock calculation	Ionization potential
$^2\Pi_g$	25.7	19.3	18.0	15.63 eV
$^2\Sigma_g^+$	29.7	23.4	20.3	17.35 eV
$^2\Pi_u$	29.5	23.1	21.9	18.46 eV

[a] Frost, D. C., McDowell, C. A., Vroom, D. A.: J. chem. Physics **46**, 4255 (1967).

with the F 2*s* orbitals and the Ar 2*s* orbital. The energy of the latter is much too low, so $\varepsilon_{2\sigma_g}$ is corrected using the F results:

$$\varepsilon_{2\sigma_g} = -1.83 + (-1.57 + 1.65) = -1.75\,.$$

Similarly, $1\pi_u$ has energy much closer to the separated atom limit $\varepsilon_{2p}^{\mathrm{F}} = -0.96$ than the united atom limit $\varepsilon_{2p}^{\mathrm{Ar}} = -9.31$, so its energy is corrected by addition of $(-0.73 + 0.96)$ to give -0.85. It has been noted [15] that the highest filled π_g and π_u orbitals resemble the separated atoms in the halogen molecules.

For $\varepsilon_{3\sigma_g}$ there is some ambiguity. The energy of -1.09 is fairly close to the separated atom $\varepsilon_{2p}^{\mathrm{F}} = -0.96$ but even closer to the united atom $\varepsilon_{3s}^{\mathrm{Ar}} = -1.08$. The former gives a correction of $+0.23$ and the latter a correction of -0.20, so only the former gives a satisfactory result. Both are included in Table 5. Except for the case just mentioned, we agree with the Hartree-Fock orbital energies to 0.08 a.u. or better. It is interesting that Recknagel [6], discussing his results for N_2, noted that certain orbitals resembled orbitals of the united atom, but not the orbitals with which they supposedly correlate. For instance, his $3\sigma_g$ MO resembled the united atom 2*s* rather than the 3*s*.

If we agree to use the corrections derived from separated atoms throughout, we may predict ionization potentials for F_2 going to several states of F_2^+. These may be compared with experimental results from photoelectron spectroscopy [16]. In Table 6 we give our results (orbital energies) without the atomic correction and with correction, the SCF results, and the experimental ionization potentials, in electron volts. The errors in the corrected values are about 30%, compared to errors of about half this for the SCF results.

As we have mentioned, orbital energies are used to predict nuclear configurations and related properties when total energies are not readily available [4]. The binding energy would be calculated as $\Sigma\varepsilon_i$ (separated atoms) $-\Sigma\varepsilon_i$ (molecule), the sums in each case running over occupied orbitals. When SCF calculations are treated this way, it may be shown [5] that the binding energy (B.E.) will be increased by 2 (B.E.) $-\Sigma Z_B \partial(\text{B.E.})/\partial Z_B$ over the difference of total energies. The sum here is over the nuclei in the molecule, and the partial derivatives are small according to the isoelectronic principle. The difference of TFD orbital energies (atoms minus molecule) is 0.75 a.u.; the difference of SCF orbital energies is 0.43 a.u. The correct binding energy is 0.062 a.u.

5. Summary and Conclusions

Orbital energies for the F_2 molecule were calculated using the TFD potential plus an exchange potential, with the overall potential replaced by $\frac{1}{2}\left(\frac{1}{r_A}+\frac{1}{r_B}\right)$ when it dropped below this. This modification assures the correct boundary condition at large distances from the nuclei. The orbital energies were in qualitative agreement with SCF values. When they are corrected by comparing atomic eigenvalues for the F atom calculated by SCF with those calculated using the TFD potential, all the eigenvalues agree to about 1/20 a.u.

An error of 0.05 a.u. ($1\frac{1}{2}$ eV) is quite comparable to the difference between ionization potentials and Hartree-Fock orbital energies, and less than the errors made in atomic calculations when the exchange interaction is replaced by the free-electron approximation, *i.e.*, an exchange potential proportional to $\varrho^{\frac{1}{3}}$. Even with corrections, however, there are several unsatisfactory features.

The order of the eigenvalues of the outer shell F_2 orbitals, which all correlate with the $2p$ atomic orbital of Fluorine, is not quite correctly given. The $3\sigma_g$ energy is incorrectly lower than the $1\pi_u$ energy. Similarly, it may be noted in Table 6 that the ${}^2\Pi_g - {}^2\Pi_u$ spacing is identical to the SCF value, but the ${}^2\Sigma_g^+$ value is incorrect relative to these. We have remarked above that the potential is certainly in error near the nuclei, where the TFD density is known to be quite incorrect. (We have shown recently [12] how this error can be largely corrected in a simple way.) The π orbitals vanish at the nuclei, the σ orbitals do not. Thus the correction will affect them differently. This must be investigated.

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Prof. Dr. J. Goodisman
Department of Chemistry
Syracuse University
Syracuse, New York 13210, USA