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Relativistic scattered wave calculations on UF$_6$

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Self-consistent Dirac–Slater multiple scattering calculations are presented for UF$_6$. These are the first such calculations to be reported, and the results are compared critically to other relativistic calculations. The results of all molecular orbital calculations are in good qualitative agreement, as measured by energy levels, population analyses, and spin–orbit splittings. The overall charge distribution is computed to be U$^{+1.5}$(F$^{-0.25}$)$_6$. Polarization functions are found to be qualitatively unimportant. A detailed comparison is made to the relativistic Xα(RXα) method of Wood and Boring, which also uses multiple scattering theory, but incorporates relativistic effects in a more approximate fashion. For the most part, the RXα results are in excellent agreement with the present results. Some differences of possible significance are noted in the lower valence and core energies.

INTRODUCTION

Uranium hexafluoride (UF$_6$) has become a prototype molecule on which to test computational methods for electronic structure problems in actinide complexes. This is due to the large amount of experimental data available and to hopes of interpreting attempts at laser isotope separation of uranium atoms. Several molecular orbital calculations have been reported. These have employed the Xα scattered wave method (with[1] or without[2,3] relativistic corrections), the Dirac–Slater discrete variational method,[4–6] and *ab initio* Hartree–Fock calculations using a relativistic effective core potential.[7(a)] Here we present results on UF$_6$ using the Dirac–Slater multiple scattering method,[8,9] along with a critical comparison of the results of these various approaches.

It seems clear that a nonrelativistic treatment of actinide complexes is seriously inadequate. First of all, the valence atomic energy levels are shifted considerably in a relativistic treatment: the uranium 6p level is ~1 eV more tightly bound in the relativistic atom, while the 5f level is less tightly bound by about 6 eV.[1] In particular, these shifts have a marked effect on the splitting between the occupied and unoccupied levels, and hence, on the interpretation of the spectrum. Secondly, the spin–orbit splittings can be large for levels that contain appreciable actinide character. For example, the first peak in the photoelectron spectrum of UF$_6$ is usually assigned to one component of the 4t_{1u} orbital, with the other spin–orbit component ~1.2 eV below contributing to a second peak.[10] Hence, relativistic effects become essential even for qualitative interpretations.

It has also become clear that perturbation calculations starting from nonrelativistic wave functions fail to describe correctly relativistic effects.[21] Changes in the core charge distributions indirectly affect the valence levels by modifying the self-consistent field. Since these indirect effects are often comparable in magnitude (and may be opposite in sign) to the direct first-order perturbation effects, the perturbation theory approach is essentially useless. Even self-consistent methods that treat the cores relativistically but use a nonrela-

tivistic method for the valence shell can give misleading results.[21] Hence, there is a definite need for computational methods that self-consistently treat all electrons in a relativistic fashion. Fortunately, a number of practical schemes that approach this goal are now available.

For our purposes, relativistic methods can be divided into two categories. In the first category are those calculations that use a Pauli Hamiltonian and calculate only the large two components of the wave function. Most commonly,[1,7,21] the mass velocity and Darwin terms may be included in the self-consistent procedure, since these terms preserve the nonrelativistic single point group symmetry. A second step then follows in which the spin–orbit operator is diagonalized in the space of these self-consistent orbitals. In practice, the spin–orbit effect is modelled by an effective one-electron operator, using either atomic spin–orbit coupling constants[7] or a $\nabla V \times \mathbf{p}$ form that is strictly applicable only to one-electron systems.[1,11] Only in this final step does one create complex wave functions that transform according to the irreducible representations of the double point group.

The second category of relativistic methods starts with the Dirac equation and retains the four-component wave function formalism throughout. Such calculations are conceptually simpler, and in principle should be more accurate than the two-step procedure outlined above. Furthermore, one then has available the small components of the wave function, which are needed e.g., to determine the response to external electromagnetic fields.[12] Unfortunately, the only *ab initio* calculations of this sort so far have used a one-center expansion technique,[13,14] a method that is applicable only to hydrides. Most other calculations have assumed an effective exchange potential, yielding the so-called Dirac–Slater problem. The wave function may be expanded in a basis set of atomiclike spinors[4–6] or may be determined by multiple scattering theory assuming spherical potentials around each atom.[8,9] The latter method has been applied with some success to a variety

of molecules,[15-18] but only recently have self-consistent calculations been carried out.[19] Hence, the present results offer the first opportunity for a critical comparison between these two Dirac–Slater computational methods. In addition, these results can serve as a check on the accuracy of quasirelativistic multiple scattering methods (Refs. 1, 20, 21, and 31), which use the same muffin-tin potential approximations and differ only in the treatment of relativistic effects.

II. DETAILS OF THE CALCULATIONS

The calculations reported here implement the method of Ref. 8. The geometry and sphere sizes were chosen to facilitate comparison with previous multiple scattering[1,3] and discrete variational[4] calculations. Thus, we set the α exchange parameter to 0.7 for the whole molecule and assumed an internuclear distance of 3.768 a.u. The sphere radii for the muffin-tin potentials were R_{out} = 5.6099, R_U = 2.6497 and R_F = 1.8407 a.u. Two calculations were done, one "minimal," with partial waves through $l = 3$ on the outer sphere and on uranium, and through $l = 1$ on fluorine. The second, "extended," calculation checked the importance of polarization functions by including partial waves through $l = 4$ and 2, respectively. This is the first calculation of UF_6 to consider the effects of these higher angular momentum contributions.

The relativistic $X\alpha (RX\alpha)$ method of Boring and Wood[1] is closest in spirit to those reported here. They use the same muffin-tin approximations, but employ an "improved Pauli Hamiltonian"[2] and include spin–orbit coupling as a final step. Indeed, this method is designed to mimic the Dirac-Slater scattered wave results, and will perhaps require less computational effort. We will see below that the $RX\alpha$ method in most respects provides a very good approximation to the full Dirac–Slater results (remembering, of course, that only the latter method gives the small components of the wave function.) Michael Boring kindly provided us with the self-consistent $RX\alpha$ potential for UF_6, so that we can compare the results for the same potential, independent of any differences in the self-consistency procedure. (In actuality, the potentials are slightly different, since the $RX\alpha$ method uses the Herman–Skillman mesh,[22] whereas we use a logarithmic mesh as in the standard atomic Dirac-Slater programs.[23] We interpolated the $RX\alpha$ potential onto our mesh and do not believe that any significant differences should arise from this change.)

It may be worthwhile to discuss briefly some features of the other calculations with which we will compare our results. The discrete variational method[4-6] uses the same Dirac–Slater model as we use, but expands the wave function in a near minimal basis of atomic spinors. Matrix elements of the Hamiltonian are evaluated by numerical procedures, which limits the precision of the one-electron energies to ± 0.1 eV.[4] This intrinsic numerical imprecision, as well as the small basis set used, should be kept in mind when detailed comparisons are to be made. The scattered-wave and discrete variational methods may be viewed as different approximations to the true Dirac–Slater results. To the extent to which they agree, both calculations may be approaching the desired result.

The *ab initio* effective core potential (ECP) calculations[7] are based on a quite different model. As with the $RX\alpha$ calculations,[1] the mass velocity and Darwin terms are included in a first (self-consistent) step, and the spin–orbit operator is added later. Since these are Hartree–Fock calculations, the one-electron energies have a different meaning than in $X\alpha$ calculations, and the two should not be compared directly. Nevertheless, we find here, as in most lighter molecules, that the general ordering of one-electron levels are very similar in the two calculations. The spin–orbit operator in the ECP calculation has an effective one-electron form fit to atomic spin–orbit coupling constants. While this procedure is a reasonable one, it should be remembered that effective spin–orbit coupling constants in molecular environments may differ considerably from those in free atoms.[11,21,24] Hence, this might be viewed as the most suspect part of the ECP calculation, although, as we show below, the spin–orbit splittings in all the calculations are in approximate agreement.

III. RESULTS

In Fig. 1 we compare the one-electron energy levels for UF_6 from four representative calculations: the *ab initio* extended core potential,[7] the relativistic $X\alpha$ scattered-wave model $(RX\alpha)$,[1] the Dirac–Slater discrete variational method (DVM),[4] and our minimum basis set Dirac–Slater scattered-wave calculations (DSW). As we mentioned above, the ECP levels cannot be directly compared to the others and we have arbitrarily added 8.1 eV to these in order to make the top occupied level coincide with the present results. (A brief report of a second DVM calculation has appeared.[6] The results were similar to those of Koelling *et al.*[4] except for the $3a_{1g}$ level, which was much lower than in any of the calculations shown in Fig. 1.)

The ordering of the levels in all the calculations are very similar. Closest agreement is found, as expected, between the DSW and $RX\alpha$ results, both of which assume muffin-tin potentials. In Table I we give the difference between the DSW and $RX\alpha$ levels using the $RX\alpha$ self-consistent potential. For the upper valence levels, with energies greater than -15 eV, these results are all within 0.1 eV of the $RX\alpha$ results. Differences between the *self-consistent* DSW and the $RX\alpha$ results are somewhat larger (see Table I), but still within the expected limits of accuracy of either calculation. For the lower valence levels, however, there are significant differences of up to ~1 eV. This may be related to the fact that the $RX\alpha$ spin–orbit matrix was constructed separately for the lower and upper valence regions and did not couple the two regions together. Another contributing factor may arise from the fact that in the uranium atom, the $RX\alpha$ method places the $6p$ orbit 0.6 eV higher than do Dirac–Slater calculations.[20] This would tend to produce molecular shifts in the direction shown, since the $1t_{1u}$ and $2t_{1u}$ levels have substantial $6p$ character (see Table II).

TABLE I. One-electron energies for UF$_6$.

Level[a]	DSW[b] min	ext	Δ_1[c]	Δ_2[d]
$5t_{1u}$ — 6u	4.46	4.39	0.05	−0.11
$5t_{1u}$ — 8u	4.52	4.46	0.12	−0.02
$2t_{2u}$ — 7u	5.97	5.74	0.09	−0.04
$2t_{2u}$ — 8u	6.16	5.97	0.09	−0.06
$1a_{2u}$ — 7u	7.02	6.75	0.09	−0.05
$4t_{1u}$ — 8u	9.78	9.58	0.15	0.17
$4t_{1u}$ — 6u	10.91	10.72	−0.04	0.00
$1t_{2g}$ — 8g	10.76	10.68	0.03	0.11
$1t_{2g}$ — 6g	10.79	10.72	0.03	0.11
$3a_{1g}$ — 6g	11.53	11.67	0.11	0.15
$1t_{2u}$ — 7u	11.53	11.35	0.03	0.09
$1t_{2u}$ — 8u	11.55	11.36	0.03	0.10
$3t_{1u}$ — 8u	12.04	11.86	0.04	0.10
$3t_{1u}$ — 6u	12.15	11.97	0.04	0.11
$1t_{2g}$ — 7g	12.14	11.96	0.03	0.11
$1t_{2g}$ — 8g	12.19	12.03	0.01	0.10
$2e_g$ — 8g	13.24	13.20	0.04	0.12
$2t_{1u}$ — 8u	22.61	22.45	0.60	0.55
$2t_{1u}$ — 6u	28.18	27.97	0.73	0.74
$2a_{1g}$ — 6g	29.54	29.51	0.09	0.17
$1e_g$ — 8g	30.11	29.99	0.07	0.15
$1t_{1u}$ — 8u	31.25	31.06	0.14	0.22
$1t_{1u}$ — 6u	34.73	34.51	1.20	1.10
$1a_{1g}$ — 6g	51.40	51.13	1.01	0.78

[a]Nonrelativistic "parent" symmetry is given to the left of the relativistic label.
[b]Negative of ground state one-electron energy (in eV).
[c]$RX\alpha$ − DSW energies (eV), where both calculations use the same potential (the self-consistent $RX\alpha$ potential).
[d]$RX\alpha$ − DSW energies (eV), where each method is separately self-consistent. The DSW minimal energies were used to calculate both Δ_1 and Δ_2.

The DVM results are also in excellent agreement with the DSW results, except for an overall difference of about 0.4 eV in the absolute magnitudes of the energy levels. The differences in level orderings affect only closely spaced levels, and such small changes should have no effect on spectral assignments. The ECP results differ from the others principally in the levels arising from $3t_{1u}$ and $1t_{2g}$, which are fluorine $2p$ combinations with a small admixture (10%–15%) of uranium character.[7(a)] In the ECP calculations, these levels are separated by 0.5 eV, while they are much more closely spaced in the other calculations. As before, these differences are too small to have any effect on conclusions drawn from the calculations.

Table I also shows the extended basis set DSW results. These are only slightly different from the minimum basis set results, the principal change being a small (~ 0.2 eV) average rise in the absolute energies. The notion that polarization functions are unimportant for
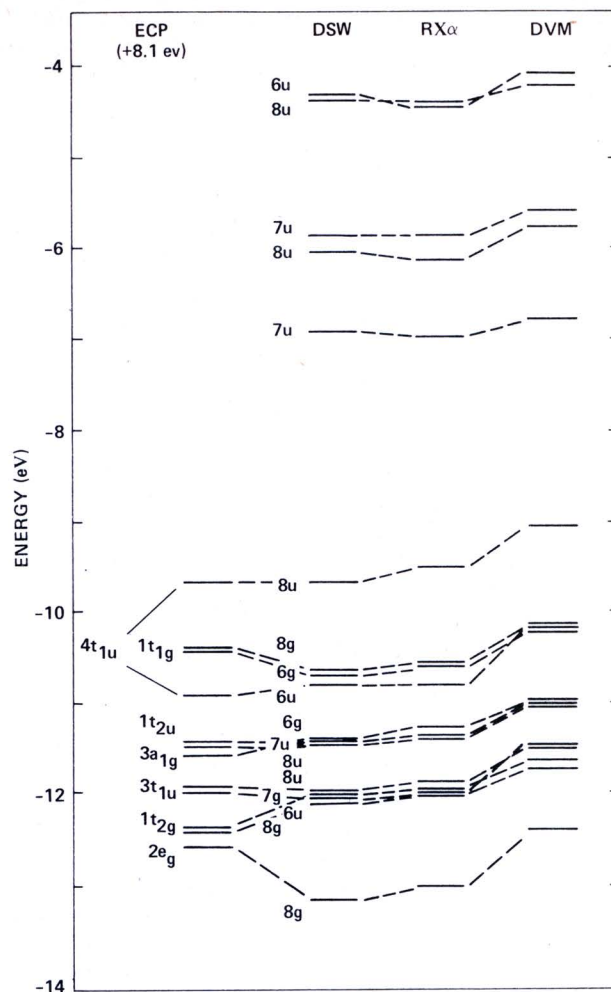

FIG. 1. One-electron energy levels for UF$_6$. Code: ECP from Ref. 7; $RX\alpha$ from Ref. 1; DVM from Ref. 4; DSW are the present minimal partial wave results.

UF$_6$ is also borne out by the charge distributions (see Table III, below) that show negligible populations in the uranium g or fluorine d orbitals).

Spin–orbit splittings can be of particular importance in understanding the electronic properties of heavy molecules. In Table II, we present the amount by which the

TABLE II. Spin–orbit splittings.[a]

Orbital	%U[b] p	d	f	ECP	$RX\alpha$	DVM	DSW min	ext
$5t_{1u}$[c]	···	···	84		−0.03	0.14	0.06	0.07
$2t_{2u}$[c]	···	···	95		0.21	0.13	0.19	0.23
$4t_{1u}$	7	···	5	1.23	1.30	1.08	1.13	1.14
$1t_{1g}$	···	0	···	0.02	0.03	0.03	0.03	0.04
$1t_{2u}$	···	···	7	0.02	0.01	0.00	0.02	0.01
$3t_{1u}$	1	···	15	0.07	0.12	0.01	0.11	0.11
$1t_{2g}$	···	11	···	0.04	0.06	0.09	0.05	0.07
$2t_{1u}$	72	···	···	6.75	5.39	5.22	5.57	5.52
$1t_{1u}$	24	···	1	2.52	2.60	3.75	3.48	3.45

[a]Values in eV.
[b]Populations from ECP calculations, Ref. 7.
[c]Unoccupied orbitals.

TABLE III. Total valence populations.[a]

| | | | DSW | |
	ECP	RXα	minimal	extended
Uranium				
$s_{1/2}$	2.21	2.34	2.35	2.31
$p_{1/2}$	⋯	⋯	2.17	2.14
$p_{3/2}$	⋯	⋯	4.08	4.05
total p	6.36	6.28	6.25	6.20
$d_{3/2}$	⋯	⋯	0.57	0.57
$d_{5/2}$	⋯	⋯	0.77	0.77
total d	1.38	1.34	1.34	1.34
$f_{5/2}$	⋯	⋯	1.29	1.28
$f_{7/2}$	⋯	⋯	1.21	1.21
total f	1.67	2.51	2.50	2.49
$g_{7/2}$	⋯	⋯	⋯	0.08
$g_{9/2}$	⋯	⋯	⋯	0.10
Fluorine				
$s_{1/2}$	1.94	2.02	2.02	2.01
$p_{1/2}$	⋯	⋯	1.76	1.75
$p_{3/2}$	⋯	⋯	3.48	3.45
total p	5.45	5.23	5.24	5.20
$d_{3/2}$	⋯	⋯	⋯	0.02
$d_{5/2}$	⋯	⋯	⋯	0.02

[a]For the scattered wave calculations, the intersphere and outer sphere charge has been partitioned as discussed in the text. The ECP results are Mulliken populations.

various nonrelativistic triply degenerate orbitals are split by the spin–orbit effect. (Although the spin–orbit effect couples levels together, to a good approximation each can be treated as deriving from a single parent level.[1]) The magnitudes of the splittings reflect the amount of metal character, since the uranium spin–orbit effect (particularly for the $6p$ orbital) is much greater than that for fluorine. From the point of view of interpretation of the uv or photoelectron spectra, the most important splitting is that of the top occupied level $4t_{1u}$. Since all the calculations place this value at 1.1–1.3 eV, this is most likely a correct picture. The other splittings are also in approximate agreement among the various calculations.

Valenc charge distributions are given in Table III. The scattered wave values represent charges inside spheres, scaled so that the total charge inside the atomic spheres is equal to the total number of electrons. This effectively partitions the intersphere and outer sphere charge among the atoms. There are other, more sophisticated ways of doing this,[24] but they generally yield similar results. Since only 3 of the 56 valence electrons are in the intersphere region, it is unlikely that the results will be sensitive to the precise method used to partition this charge. ECP results shown are based on the Mulliken population scheme.

Qualitatively, the results are all in good agreement. The only significant difference between the ECP and the scattered-wave calculations lies in the partitioning of charge between the uranium $5f$ and fluorine $2p$ orbitals. Examination of the $RX\alpha$ charge distributions for in-

dividual orbitals shows that the occupied $3t_{1u}$, $4t_{1u}$, and $1t_{2u}$ orbitals have more $5f$ character than the ECP results, while the unoccupied $2t_{2u}$ and $5t_{1u}$ orbitals have less $5f$ character. This leads to a less positive metal in the scattered-wave calculations ($U^{+1.5}$) than in the ECP($U^{+2.4}$). This is most likely due in large part to the different ways of partitioning the overlap charge in the two calculations; it is a general rule that scattered-wave calculations yield a less positive metal than do Hartree–Fock calculations.[11,25] In spite of this difference, though, the scattered-wave calculations are remarkably similar to those obtained from the ECP calculations, and give the same picture for the molecular orbital structure of UF$_6$.

Core energy levels are shown in Table IV and compared to Dirac–Slater (DS) or $RX\alpha$ calculations on the uranium atom. The DSW results show a smooth downward shift compared to the atomic calculation, consistent with what one would expect for a slightly positive metal ion. The $RX\alpha$ calculations (M. Boring, personal communication) have nearly identical chemical shifts, even though the absolute value of core energy levels differs from the DSW results. This difference is most pronounced for the $1s$ and $2s$ orbitals, and is reflected in Fig. 2, which shows the difference between the $RX\alpha$ and DSW self-consistent potentials for UF$_6$. In the valence region ($r \gtrsim 0.4\,a_0$) of uranium, the two potentials are within 0.5 eV of each other, which is consistent with the close agreement of the valence energy levels seen above. (The fluorine potentials are in even closer agreement, with the maximum deviation in the valence region being about 0.1 eV.) In the uranium core region, however, there are large discrepancies, which appear to be reflected in the core energies. It should be noted that the DSW logarithmic mesh begins at $r = 1.2 \times 10^{-4} a_0$, while the $RX\alpha$ mesh starts at $4.5 \times 10^{-4} a_0$. The $1s$ and $2s$ levels may be very sensitive to this difference or to the precise way in which the radial differential equation is started at $r = 0$.

TABLE IV. Core energy levels.[a]

| | | Chemical shift | |
Level	DSW	DSW[b]	RXα[c]
$1s$	−8513.25	−0.40	⋯
$2s$	−1590.85	−0.44	−0.44
$2p$	−1346.51	−0.43	−0.43
$3s$	−402.01	−0.48	−0.48
$3p$	−333.00	−0.48	−0.48
$3d$	−262.66	−0.48	−0.47
$4s$	−102.73	−0.47	−0.47
$4p$	−79.84	−0.47	−0.46
$4d$	−53.84	−0.47	−0.46
$4f$	−27.82	−0.47	−0.47
$5s$	−23.16	−0.46	−0.45
$5p$	−15.95	−0.45	−0.43
$5d$	−7.63	−0.42	−0.41

[a]Values in Rydberg units.
[b]Present results minus Dirac–Slater atom results.
[c]$RX\alpha$ results from Ref. 1 minus $RX\alpha$ atomic results.

These core energy differences apparently have little effect on the shape of the orbitals, as evidenced from the calculated spin–orbit splittings, shown in Table V, In both the Dirac–Slater and $RX\alpha$ methods, the molecular values are essentially identical to the atomic values. The largest differences between the calculations are in the $2p$ and $3d$ orbitals and are probably related to the approximate way in which the spin–orbit operator is incorporated into the $RX\alpha$ method.

IV. DISCUSSION

Our principal purpose in this paper has been to illustrate in some detail the level of agreement that may be expected from different molecular orbital approaches to molecules containing heavy atoms. All four of the schemes discussed here have been applied to a small, but growing number of molecules (see the review by Pyykkö[26]). Common calculations on UF₆ provide an excellent opportunity for cross comparisons. The calculations reported here are the first self-consistent DSW ones, but a brief report of earlier non-self-consistent results on UF₆ has appeared.[27]

For this molecule, all the calculations agree to within their expected error limits. For qualitative discussions of the bonding or for semiquantitative assignments of spectra, all should be equivalent. Indeed, it is for this reason that we do not discuss experimental results, and refer the interested reader to the analyses based on earlier calculations.[1–7] Here we will consider only the relative merits of different approaches.

From the point of view of computational efficiency, the scattered-wave methods ($RX\alpha$ and DSW) are clearly superior to the linear combination of atomic orbitals (LCAO) methods, and this discrepancy will be even larger for bigger molecules. The DVM results were limited to a near-minimal basis set, and even at this level have significant residual numerical errors in the one-electron energies. Improvements in computer codes may be able to alleviate this situation somewhat. By making

TABLE V. Uranium core-level spin–orbit parameters.[a]

| | Dirac–Slater | | $RX\alpha$ | |
Label	atom[b]	UF₆[c]	atom[b]	UF₆[d]
2p	187.5	187.71	185.2	185.2
3p	43.2	43.26	43.3	43.35
4p	11.3	11.30	11.3	11.30
5p	2.68	2.70	2.68	2.69
3d	5.26	5.27	5.43	5.43
4d	1.24	1.25	1.28	1.28
5d	0.24	0.241	0.25	0.248
4f	0.23	0.232	0.24	(d)

[a]The spin–orbit parameter is $2(\mathcal{E}_{nlj+} - \mathcal{E}_{nlj-})/(2l+1)$. Values in Rydberg units.
[b]Reference 20.
[c]Minimal and extended results are identical to the number of significant figures shown.
[d]Reference 1; the value for the $4f$ orbital is not given.

optimal use of symmetry, Hay et al.[7] were able to calculate the two-electron integrals needed for the ECP calculation in 4 min on a CDC 7600 computer. Some additional time is required for the self-consistent-field (SCF) iterations, and the generation of the core potential itself is a major undertaking, albeit one that needs to be done only once. By contrast, the $RX\alpha$ method requires about 3 sec and the DSW about 8 sec per iteration, again on a CDC 7600. About 20–30 iterations are required to achieve self-consistency, so that total computational times are on the order of 1–4 min. The extended basis set DSW calculations are about twice as time consuming as the minimal basis set calculations. Both the $RX\alpha$ and DSW timings could be decreased by ~40% by making better use of symmetry (based on unpublished improvements in nonrelativistic octahedral complexes). For larger molecules, or for calculations including polarization functions, the advantage of the scattered-wave method becomes much more pronounced.

The question of the intrinsic accuracy of the various approaches is more difficult to assess. The high symmetry, close-packed geometry of UF₆ is favorable for multiple-scattering calculations, although nonrelativistic calculations indicate that even more open, planar structures can be handled satisfactorily. The ab initio calculations have the advantage that one can add (nonrelativistic) configuration interaction in order to study states not well represented by single determinants or to estimate correlation energy effects. Effective exchange potentials, on the other hand, open the possibility of making Slater transition state calculations,[28] which can be very useful for interpretative purposes. In the future, computer codes to perform ab initio calculations based on the Dirac equation may become available,[29] which would make possible benchmark calculations. For now, it appears from cross comparisons of the type made here, that multiple-scattering calculations should be adequate for the purposes for which they are usually used, e.g., as an aid for the interpretation of spectra or in the discussion of general bonding trends.
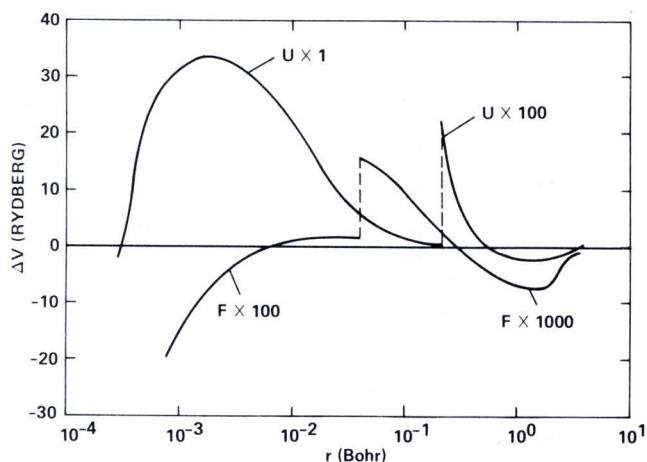

FIG. 2. Plot of the present DSW minimal partial wave self-consistent potential minus the $RX\alpha$ self-consistent potential (Ref. 1). The spherically averaged potentials in the uranium and fluorine spheres were used to construct the figure. Some of the ΔV curves have been scaled for better clarity.

Finally, we may compare the merits of the $RX\alpha$ and DSW approaches, both of which employ a scattered-wave formalism. The $RX\alpha$ method was designed to be an efficient approximation to the DSW method and one that could easily be incorporated into existing nonrelativistic programs. Until now, only indirect assessments of its accuracy could be made, since self-consistent DSW codes were not available. The present results support the earlier claims[1,20,21] of accuracy for the $RX\alpha$ method (except for the core energies) and suggest that it will be about three times faster than the DSW method. However, the Dirac method is more automatic, in that it does not require a choice of what orbitals to include in the second, spin-orbit step, and it also allows for indirect (self-consistent) effects arising from the spin-orbit operator. Perhaps the most important advantage of the DSW model was not illustrated here: the availability of the small components of the wave function. We are currently writing computer codes to make use of this information.

Our understanding of relativistic effects in molecules is increasing very rapidly following a long period of neglect.[26,30] Nonrelativistic multiple-scattering calculations have proved to be extremely useful to inorganic chemists and solid-state physicists studying the lighter transition metals. Now that the analogous programs based on the Dirac equation are available, there is good reason to hope that heavier systems can come under similar scrutiny and that trends in the columns of the periodic table can be more fully understood.

ACKNOWLEDGMENTS

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