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RELATIVISTIC SELF-CONSISTENT MOLECULAR ORBITAL CALCULATION FOR UF$_6$

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The relativistic self-consistent molecular orbital calculation was made for UF$_6$ in the Dirac-Slater model. The one-electron energies, excitation energies and the effects of relativity are presented.

Uranium hexafluoride UF$_6$ is of extreme interest in nuclear industries. Only a few molecular orbital(MO) calculations in non-relativistic approximation have been reported[1,2]. Although, for the molecule containing such a heavy atom as U, one should certainly consider the effect of relativity, the relativistic MO calculation of UF$_6$ has not yet been made until now. In order to obtain reliable information on molecular properties such as the orbital energy, excitation energy and the electronic structure of this molecule, we performed the relativistic self-consistent MO calculation in the discrete variational(DV) scheme based on the Dirac-Slater(DS) model, using numerical basis. The computational method employed here has been successfully applied to several molecules[3,4] and UO$_2^{++}$ [5] in the approximate self-consistent-field(SCF), the self-consistent-charge(SCC) method.

In this letter we report the relativistic one-electron energies of UF$_6$ and discuss about the relativistic effects of this molecule. The excitation energies are also estimated and compared with the experimental absorption spectrum[6].

Molecular geometry of UF$_6$ was determined from the experimental data[7] as Oh symmetry with the bond distance of U-F being 1.999 A. A numerical basis set($5f_{5/2}$, $5f_{7/2}$, $6s_{1/2}$, $6p_{1/2}$, $6p_{3/2}$, $6d_{3/2}$, $6d_{5/2}$ and $7s_{1/2}$ for U, and $2s_{1/2}$, $2p_{1/2}$ and $2p_{3/2}$ for F) was used for the calculation. The calculation was done with the exchange parameter α=0.70 for all atoms and with the number of DV sample points(numerical intergration grid) N=1000.

Firstly, a non-relativistic DV-Xα calculation in the spherical averaged SCF(SCFS) procedure[8] was performed in the same computational conditions as stated above. The valence levels are given in Fig. 1. Two multiple scattering(MS)-Xα results are also given: MS-Xα-2[2] in muffin-tin potential and MS-Xα-1[1] with the overlapping sphere scheme. The feature of our (SCFS) levels resembles well MS-Xα-1 except

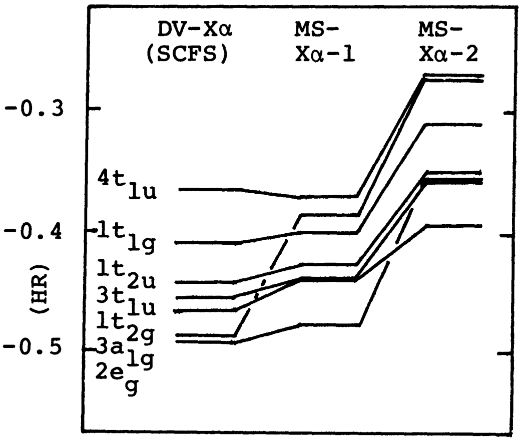

Fig. 1 Non-relativistic valence levels of UF$_6$

$3a_{1g}$.

The SCC one-electron energy levels of UF_6 for both of the relativistic and non-relativistic calculations are given in Fig. 2. The levels are classified into two parts in terms of the symmetry for the inversion: gerade to left side and ungerade to right. The correlation between the non-relativistic and the relativistic levels was determined by the relation of the irreducible representation between single and double groups and by the comparison of the wavefunctions. The highest occupied orbital is $4t_{1u}$ for non-relativistic, while the corresponding $5\Gamma_8^-$ is for relativistic. The main orbital component for each level is indicated on the center of the figure. For example, all the higher valence levels($3\Gamma_6^+ \sim 4\Gamma_8^+$ and $3\Gamma_6^- \sim 5\Gamma_8^-$) are mainly localized to the F $2p_{1/2}$ and/or $2p_{3/2}$ orbital and the lower excited levels ($2\Gamma_7^- \sim 5\Gamma_6^-$) to the U $5f_{5/2}$ and/or $5f_{7/2}$. A significant discrepancy between the two calculations was observed for 5f orbital population, though the orbital populations for corresponding levels resemble rather well. The number of 5f electrons is 3.35 for non-relativistic calculation and 1.76 for relativistic one.

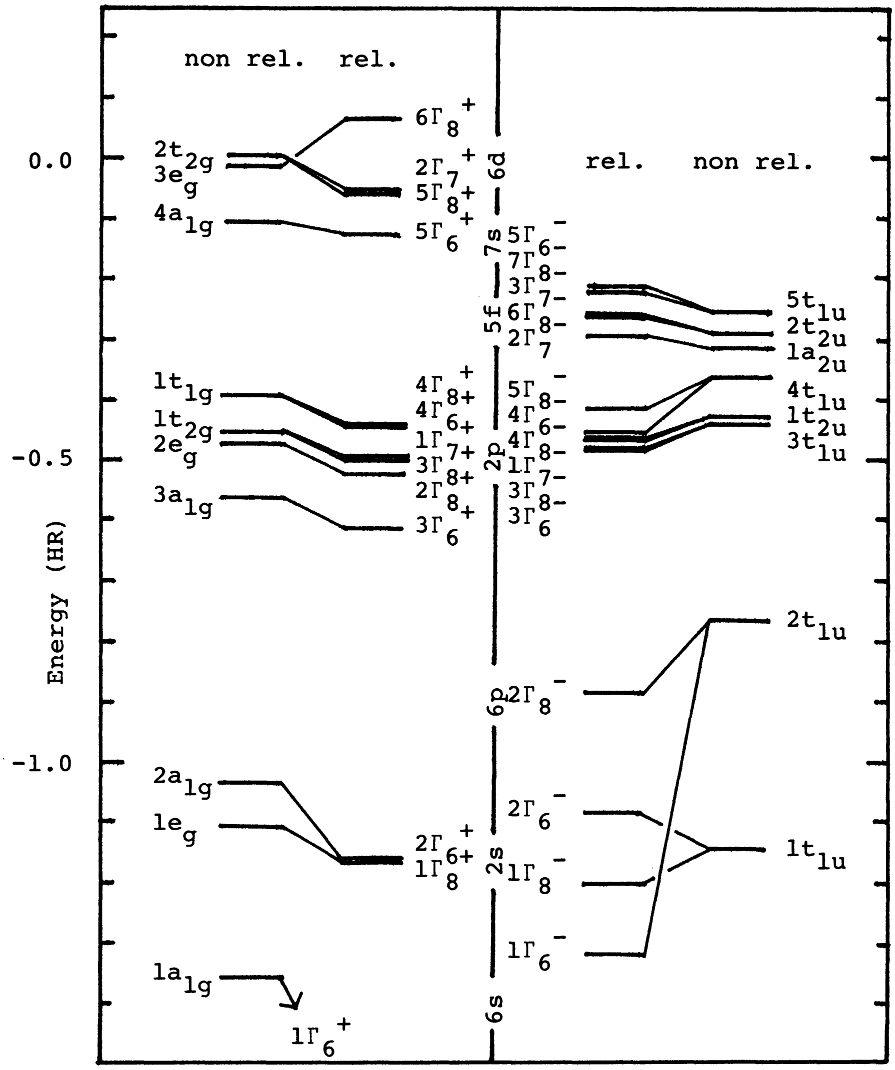

Fig.2 SCC one-electron energy levels of UF_6 for relativistic and non-relativistic calculations

The decrease of the 5f electrons is mainly due to the indirect relativistic effect, which is due to the change of the electron shielding, as seen in the case of free atom[9]. The change of the 5f orbital population directly affects to the atomic charge distribution, so that the U charge in the relativistic calculation is reduced from +1.25 to +2.72 when compared with non-relativistic one.

The other relativistic effects are also seen unambiguously in Fig. 2: (a) the energy lowerings of about 0.05 HR for the higher valence levels and (b) the energy splittings of the several levels, especially large for $1t_{1u}$, $2t_{1u}$ and $4t_{1u}$. The shift of the valence levels is due to the direct and indirect effects. The rather large energy splittings for $1t_{1u}$, $2t_{1u}$ and $4t_{1u}$ levels are ascribed to the spin-orbit coupling effect of U 6p orbital(ξ_{6p}=0.33 HR for neutral atom), since these relativistic and non-relativistic levels contain 6p orbital components. The splitting energy is correlated to the amount of 6p orbital populations and the interaction between the orbitals belonging to the same representation, i.e. Γ_6^- or Γ_8^-.

Fig. 3 shows the comparison of the experimental UV absorption spectrum[6] and theoretical excitation energies of the charge transfer transitions from F 2p to U 5f estimated by both relativistic and non-relativistic calculations. The experimental spectrum of UF_6 shows the strong bands in the UV region at about 215,

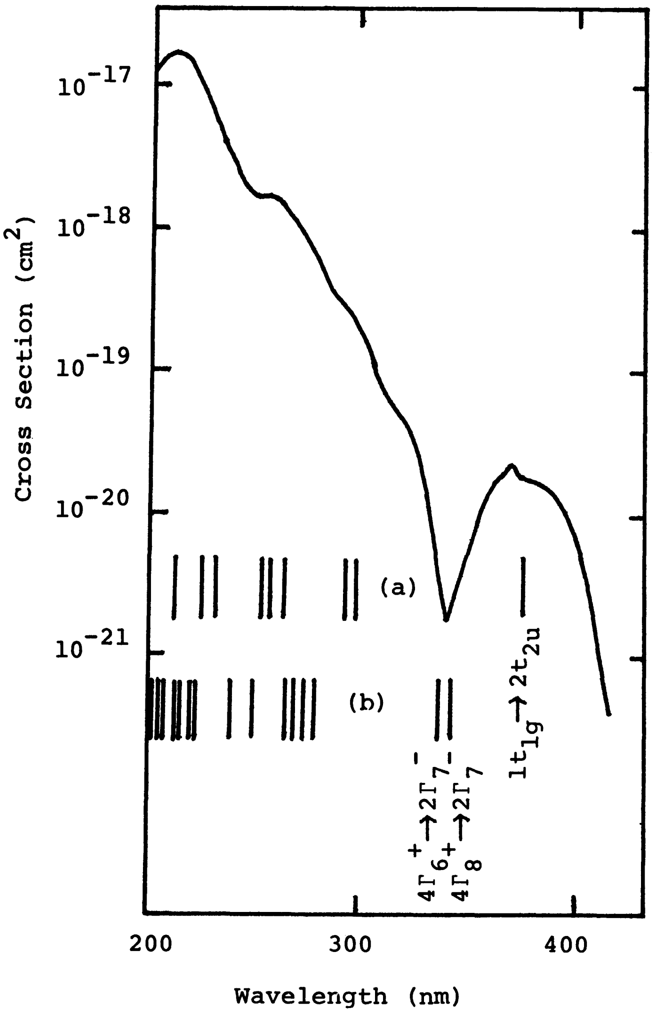

Fig. 3 Absorption spectrum of UF_6 and theoretical excitation energies
(a) Non-relativistic.
(b) Relativistic.

260, 300 and 320 nm(allowed transition) and weak one with the structure at about 370 nm(probably forbidden). The non-relativistic excitation energies seem to be in extremely good accordance with the experimental peaks, but the low intensity of the band in the visible region can bot be explained by the $1t_{1g} \rightarrow 2t_{2u}$ transition which is dipole allowed. The spectral feature of the relativistic excitation energies reproduced very well the experimental data in more reliable manner, though all the energies are uniformly shifted about 0.3 eV higher. The lower transitions from the $4\Gamma_6^+$ and $4\Gamma_8^+$(split from $1t_{1g}$ level by a small spin-orbit coupling of F 2p) to $2\Gamma_7^-(1a_{2u})$ are all dipole forbidden. Therefore, the relativistic calculation gives a satisfactory interpretation for the low intensity in the visible band, whose structure can also be assigned to the spin-orbit splitting of F 2p.

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