

ELECTRONIC STRUCTURE OF UF₅

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Non-relativistic and relativistic self-consistent Hartree–Fock–Slater and Dirac–Slater models have been used to calculate one-electron energy levels and ionization energies for UF₅. The calculations were performed in an assumed structure of C_{4v} symmetry with the uranium atom at the center of mass of the molecule. The spacing and level ordering are compared with earlier results obtained with the MS X α method using the muffin-tin approximation. Connections with the multiphoton isotope separation scheme of UF₆ are discussed.

1. Introduction

The increased demand for enriched uranium as a fuel source has directed a large amount of research in recent years towards the development of more efficient and economic isotope separation methods. In conventional diffusion and gas centrifugation procedures the isotopes are separated utilizing the mass dependence of the diffusion rate constants. However, a number of laser separation schemes [1] have been proposed in which the isotopes are separated by exploiting excitation schemes where selectivity is achieved due to the different atomic and molecular isotope shifts. A tunable and sufficiently monochromatic laser is matched to the absorption line of an atom or compound containing the desired isotope while those atoms and compounds with other isotopes are unaffected. The excited atom or compound is then ionized or brought to dissociation by additional excitations with another light-source such as, for example, a laser. In another method known as the multiphoton dissociation technique [2] an intense laser beam from, for example, a CO₂ laser acts upon molecules, which are dissociated by absorption of more than thirty infrared quanta. In particular considerable work has been

performed on SF₆. In a molecular beam study of the multiphoton dissociation of SF₆ the dissociation products have been analyzed with a quadrupole mass filter and found to be SF₅ and F [3]. Another means of detection would be to monitor the change in optical or infrared absorption spectra.

Of all currently known uranium compounds the molecule UF₆ exhibits the highest vapor pressure and is a strong candidate for laser isotope separation [4]. Recently, multiphoton absorption in UF₆ with 16 μ m wavelength has been reported for the first time [5]. In view of the recent molecular beam study of multiphoton dissociation of SF₆ into the products of SF₅ and F it would therefore be of great interest to study the electronic structure of UF₅ which would appear as the corresponding product in the separation of UF₆.

The electronic structure of UF₆ has been the subject of experimental and theoretical investigations for a long period [6]. Recently, non-relativistic [7,8] as well as relativistic calculations [9] within the Hartree–Fock–Slater (HFS) and Dirac–Slater (DS) models have been performed. Also non-relativistic MS X α calculations have appeared [10,11]. The theoretical relativistic transitions [9] were found to be in good

agreement with the experimental data obtained by Lewis et al. [6].

2. Computational method

The calculations can briefly be described as follows [12]. The relativistic one-electron hamiltonian is given by

$$h = c\alpha \cdot p + \beta mc^2 + V(r),$$

where $c\alpha \cdot p + \beta mc^2$ are the kinetic and rest energy operators. $V(r)$ is the potential energy operator which can be divided as usual into the Coulomb and exchange terms. This last part is obtained from the molecular charge density using the Slater $X\alpha$ method with the exchange parameter $\alpha = 0.70$. A variational method is used to find the molecular wavefunctions, which are approximated by a linear combination of symmetry orbitals constructed from atomic numerical basis functions. The basis set for uranium have been generated in the $5f^36d7s^2$ atomic configuration. The Hartree-Fock-Slater, Dirac-Slater and overlap matrix elements were evaluated by using the discrete variational method as described in earlier calculations [13]. The molecular potential was determined in the successive iterations, from Mulliken gross orbital populations for the basis functions. These populations were spherically averaged and the molecular potential was constructed from the spherical charges on the constituent atoms. Self-consistency was obtained when the input and output orbital charges were equal. This procedure does not imply spherical symmetry of the molecular potential as for example in the "muffin-tin" form used in the multiple scattering method (MS $X\alpha$) [14]. A rather good agreement has generally been obtained between experimental and theoretical ionization energies [7-9,12].

3. Results

The calculations were performed in the proposed geometry of C_{4v} [15] with the uranium atom at the center of mass of the molecule. All the U-F bond lengths have been assumed to be the same and equal to the experimental bond length $R(U-F) = 3.768$ au of UF_6 [16]. A structure of a square pyramid with

the uranium atom above the F atom equatorial plane has also been predicted by Krohn et al. [17] in the analysis of the infrared spectrum obtained by Paine et al. [18].

Different theoretical eigenvalues in the valence region are presented in fig. 1. To the left in the figure are the MS $X\alpha$ results of Maylotte et al. [11] which were calculated using the same bond length. These values may be compared with the non-relativistic HFS eigenvalues in the middle of the figure and the corresponding relativistic ones to the right obtained with in this work. The splitting of the non-relativistic

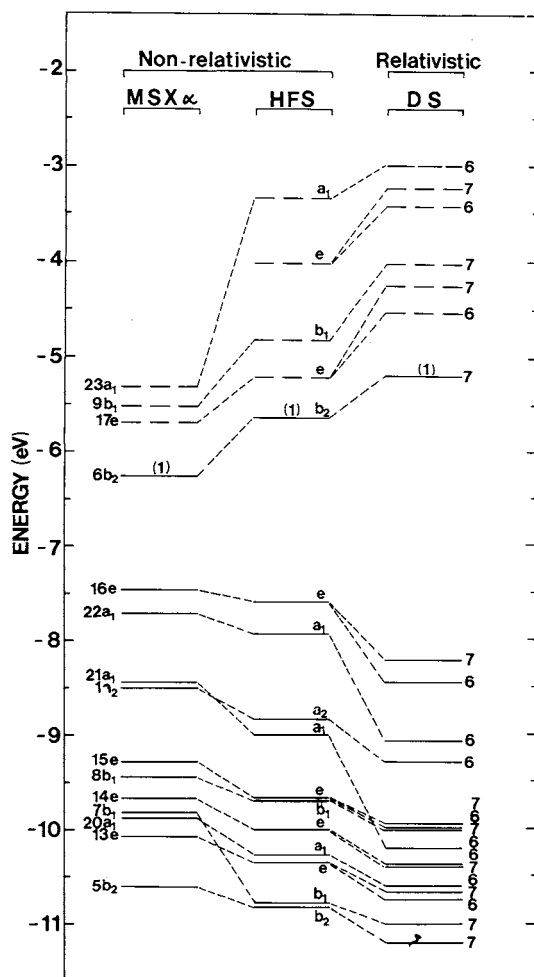


Fig. 1. Comparison of molecular eigenvalues for UF_5 calculated with the multiple scattering $X\alpha$ (MS $X\alpha$), discrete variational Hartree-Fock-Slater (HFS) and relativistic Dirac-Slater (DS) methods.

levels into the relativistic ones have been indicated by using the compatibility relations between the single and double groups. The MS X α and HFS methods give the same level ordering for most levels while the valence band in the HFS and DS methods is broader compared with what is the result of the MS X α method. It may be noticed further how the deeper valence levels in the DS method are more strongly bound compared with the HFS result while the reverse holds for the last occupied b_2 level and the optical levels. These differences are due to the mixing of the more tightly bound molecular levels originating from the atomic $6s$, $6p_{1/2}$, $6p_{3/2}$ levels and due to the expanded $5f_{5/2}$ and $5f_{7/2}$ atomic levels in the relativistic states compared with the non-relativistic one, which give rise to less bound molecular levels. Calculations have also been performed changing the position of the uranium atom within the C_{4v} symmetry retaining the same bond length as before i.e. $R(U-F) = 3.768$ au. Calculation with the uranium in the plane and at a distance of 1.500 au above the plane compared with the position of 0.942 au for the earlier calculation changed the eigenvalues in the valence region in the order of 0.1–0.4 eV.

Knowledge about the optical spectra of UF_5 would be useful for monitoring the presence of UF_5 in the multiphoton dissociation process. Some allowed transitions which have been evaluated from the difference in orbital energies are given in table 1. It may be noticed how the relativistically evaluated wavelengths are quite different compared with the non-relativistic ones, mainly due to the broader valence band. In the earlier analysis of UF_6 [9] good agreement with the experimental data of Lewis et al. [6]

Table 1
Some orbitally allowed transitions between states in the valence region of UF_5

Transition	Wavelength (nm)		
	MS X α	HFS	DS
$6b_2 \rightarrow 17e$	2121	2954	1824 1292
$6b_2 \rightarrow 18e$		756	697 633
$16e \rightarrow 6b_2$	1037	639	413 388

was obtained. However, the wavelengths evaluated for UF_5 are somewhat uncertain since relaxation effects have not been included. For UF_6 transition state calculations [9] increased the energy for the optical transitions by 0.4–0.6 eV compared with those evaluated from the difference in ground state eigenvalues.

The ionization potential for UF_5 determined from electron impact measurements [19] has been found to be 11.29 eV which should be compared with the eigenvalue of 5.4 eV and a relativistic transition state calculation which gave 9.7 eV. About the same discrepancy between the theoretical and experimental ionization energy was also found for UF_6 in the earlier calculations [7,9]. This degree of agreement between the theoretical and experimental ionization potential support therefore a structure of C_{4v} for UF_5 . There is however some uncertainty about the actual bond-length in UF_5 which in this work has been assumed to be the same as in UF_6 . Further calculations to investigate the effect of changing the bond-length and to evaluate the total energy for different geometries are now in progress to give a more precise answer of the structure of UF_5 .

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