

Relativistic Molecular Orbital Calculations for Diatomic Molecules

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The relativistic molecular orbital calculations have been made for diatomic molecules by the use of the discrete variational $X\alpha$ method. The validity of the method has been tested for CO molecule and good agreement is obtained between the relativistic and nonrelativistic calculations. The relativistic results for UO molecule are compared with the nonrelativistic ones and the importance of the relativistic effects is indicated.

KEY WORDS: Relativistic molecular orbital calculation/ Discrete variational $X\alpha$ method/ Diatomic molecule/

I. INTRODUCTION

The importance of the relativistic effects in the electronic structures of molecules and chemical bondings has been recognized for many years. With recent advance in high-speed computers with large memory capacity, the relativistic molecular orbital calculations have received special attention.¹⁾ The relativistic effects appear as the shift of the energy levels, the spin-orbital splitting, and the modifications of wave functions and potentials due to change in inner-shell electron shielding.

In recent years, the discrete variational (DV) $X\alpha$ method has been applied to the nonrelativistic problems²⁾ and found to be very useful to obtain the informations on electronic structures of molecules. The main advantage of this method is the minimal number of basis functions. The relativistic extension of this method, based on the Dirac-Slater (DS) equations, has already been developed³⁾ and used for chemical compounds of heavy elements, such as actinides, with encouraging results.⁴⁻⁹⁾

In the present work, the relativistic calculations for electronic structures of the diatomic molecules have been performed by the DV- $X\alpha$ method. In order to test the validity of the method, the calculations are made for CO molecules, in which the relativistic effects are considered to be negligible. Then the relativistic molecular orbital calculations for UO molecule are performed and compared with the results of the nonrelativistic DV- $X\alpha$ method.

II. COMPUTATIONAL METHOD

In the relativistic DV- $X\alpha$ method, the one-electron molecular Hamiltonian is written by

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$$H = c \boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2 + V(\mathbf{r}). \quad (1)$$

Here c is the velocity of light in vacuum, m is the rest mass of the electron, \mathbf{p} is the usual momentum operator, and $\boldsymbol{\alpha}$ and β are the velocity operators

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix},$$

and

$$\beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix},$$

where $\boldsymbol{\sigma}$ is the 2×2 Pauli spin matrix and I is the 2×2 unit matrix.

The molecular potential $V(\mathbf{r})$ is constructed as the sum of the Coulomb and exchange potentials. The exchange potential is approximated by an expression proportional to the cubic root of the local charge density,¹⁰⁾

$$V_{\text{ex}}(\mathbf{r}) = -3\alpha \left| \frac{3}{8\pi} \rho(\mathbf{r}) \right|^{1/3}. \quad (2)$$

The exchange scaling parameter is taken to be $\alpha=0.7$ throughout the present work.

The molecular wave functions is expanded in terms of symmetry orbitals and each symmetry orbital is obtained as a linear combination of relativistic four-component atomic orbitals. The numerical wave functions for atomic orbitals are given as solutions of DS equations for free atoms and used as basis functions.

Using the molecular wave functions thus constructed, the secular equations is derived by the variational principle as

$$\mathbf{HC} = E \mathbf{SC}, \quad (3)$$

where H_{ij} and S_{ij} are the Hamiltonian and overlap matrices, respectively. These matrix elements are calculated by the use of the DV numerical integration scheme, i.e. the integral is evaluated as the weighted sum of integrand values at sampling points distributed randomly in real space. The eigenvalues E and eigenvectors \mathbf{C} converge rapidly with the number of sampling points N . In the present calculations, N is chosen to be 1500.

We use the self-consistent-charge (SCC) approximation to the complete self-consistent-field method. In the SCC method, overlap charges are partitioned into atomic charge densities by the use of the Mulliken population analysis.¹¹⁾ The atomic densities are spherically averaged and employed to give numerical basis functions and molecular potential for the next iteration. These procedures are repeated until orbital populations fulfill the convergence criterion.

III. RESULTS AND DISCUSSION

In the present work, the relativistic DV- $X\alpha$ calculations have been made for diatomic molecules, CO and UO. For comparison, the nonrelativistic DV- $X\alpha$ method²⁾ has also been used for the same molecules with the same input data. All

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Table I. Orbital populations for CO molecule.

Element	AO	Relativistic	Nonrelativistic
C	1s	2.000	2.000
	2s	1.579	1.579
	2p _{1/2}	0.712	2.135
	2p _{3/2}	1.421	
	net charge	+0.288	+0.286
O	1s	2.000	2.000
	2s	1.842	1.840
	2p _{1/2}	1.484	4.446
	2p _{3/2}	2.962	
	net charge	-0.288	-0.286

Table II. Nonrelativistic energy eigenvalues (eV) and orbital components (%) for CO.

MO	Eigenvalue (eV)	O			C		
		1s	2s	2p	1s	2s	2p
1σ	-512.00	100					
2σ	-272.32				100		
3σ	-29.11		66	11		11	12
4σ	-13.75		25	54		21	
1π	-11.51			72			28
5σ*	-9.62		1	14		46	39
2π	-2.16			28			72
6σ	14.58		8	21		21	50

* Highest occupied molecular orbital.

Table III. Relativistic energy eigenvalues (eV) and orbital components for CO.

MO	Eigenvalue (eV)	O				C			
		1s	2s	2p _{1/2}	2p _{3/2}	1s	2s	2p _{1/2}	2p _{3/2}
1S _{1/2}	-512.75	100				100			
2S _{1/2}	-272.78								
3S _{1/2}	-29.42		66	4	7		11	4	8
4S _{1/2}	-13.97		25	18	36		21		
5S _{1/2}	-11.73			48	24			19	7
1S _{3/2}	-11.71				72				28
6S _{1/2} *	-9.84		1	4	9		47	13	26
7S _{1/2}	-2.41			19	9			48	24
2S _{3/2}	-2.39				28				72
8S _{1/2}	13.99		8	7	14		21	17	33

* Highest occupied molecular orbital.

the numerical calculations have been carried out on the FACOM M-382 computer in the Data Processing Center of Kyoto University.

First, we tested the validity of the relativistic method for CO molecule. Owing to small atomic numbers, the relativistic effects are negligible in this molecule. The interatomic distance is set to be 2.132 bohr.¹²⁾ In Table I, the orbital populations

Table IV. Orbital populations for UO molecule.

Element	AO	Relativistic	Nonrelativistic
U	5f _{5/2}	3.375	4.714
	5f _{7/2}	0.446	
	6s	1.559	1.961
	6p _{1/2}	1.969	5.620
	6p _{3/2}	3.787	
	6d _{3/2}	1.058	0.640
	6d _{5/2}	0.564	
	7s	0.315	0.075
	7p _{1/2}	0.029	0.101
	7p _{2/2}	0.062	
	net charge	+1.004	+0.993
O	2s	1.953	1.948
	2p _{1,2}	1.675	5.045
	2p _{3/2}	3.368	
		net charge	-1.004

Table V. Nonrelativistic energy eigenvalues (eV) and orbital components for UO.

MO	Eigenvalue (eV)	U						O	
		5f	6s	6p	6d	7s	7p	2s	2p
15σ	-26.50		91	1				5	2
16σ	-18.21		5	9	5			80	1
9π	-14.99			99					1
17σ	-8.39	4		56		4		13	22
10π	-3.59	7			9				84
18σ	-2.33	18		13	7	1	4		57
2φ*	-0.21	100							
5δ	-0.21	95			5				
11π	-0.004	86			12				2
6δ	2.16	5			95				
19σ	3.40	49		7		34	10		
12π	4.27	7		1	74		6		12
20σ	6.32	3		1	36	44	13		2
13π	9.60				4		94		1
21σ	10.72	27		18	14	17	5	3	16
22σ	20.13		1		30	1	68		

* Highest occupied molecular orbital.

for CO molecule obtained by the relativistic and nonrelativistic calculations are shown together with the net charge on each atom. Table II indicates the nonrelativistic energy eigenvalues and orbital components, while the relativistic values are listed in Table III. It is clear from the tables that both relativistic and nonrelativistic calculations give practically same results.

In order to demonstrate the relativistic effects, the calculations have been made for UO molecule. The U-O distance in UO gas molecule is known to be 3.7 bohr.¹³⁾ The relativistic and nonrelativistic values for orbital populations in UO are shown in Table IV. It can be seen that the net charge on the U atom in the relativistic case is slightly larger than in the nonrelativistic case, but almost equal to each other. The orbital populations for O atom are same for both cases. On the other hand, for U atom the 6*d* and 7*s* increase in the relativistic case, while the 5*f* population decreases.

The energy eigenvalues and orbital components are listed in Table V for the nonrelativistic case and in Table VI for the relativistic case. Comparison of the

Table VI. Relativistic energy eigenvalues (eV) and orbital populations (%) for UO.

MO	Eigenvalue (eV)	U						O	
		5 <i>f</i>	6 <i>s</i>	6 <i>p</i>	6 <i>d</i>	7 <i>s</i>	7 <i>p</i>	2 <i>s</i>	2 <i>p</i>
23 <i>S</i> _{1/2}	-32.21		2	95				1	1
24 <i>S</i> _{1/2}	-21.57		48	4		15		25	6
13 <i>S</i> _{3/2}	-19.23			99					1
25 <i>S</i> _{1/2}	-19.03	1	16	24	5		2	51	
26 <i>S</i> _{1/2}	-11.43	7	2	57				21	13
27 <i>S</i> _{1/2}	-4.37	4			11				84
14 <i>S</i> _{3/2}	-4.25	5			11				84
28 <i>S</i> _{1/2}	-3.46	19	1	6	7		3		63
15 <i>S</i> _{3/2}	-0.31	60			40				
6 <i>S</i> _{5/2} *	-0.04	92			8				
29 <i>S</i> _{1/2}	0.15	70			29		1		
7 <i>S</i> _{5/2}	0.40	56			44				
16 <i>S</i> _{3/2}	0.48	58			42				
2 <i>S</i> _{7/2}	0.79	100							
17 <i>S</i> _{3/2}	0.91	53			46				
8 <i>S</i> _{5/2}	1.39	51			49				
30 <i>S</i> _{1/2}	1.54	17			18	1	61		3
18 <i>S</i> _{3/2}	2.95	20			42		29		9
31 <i>S</i> _{1/2}	3.13	24			43	3	29		1
32 <i>S</i> _{1/2}	4.10	18		2	38	8	20		13
19 <i>S</i> _{3/2}	5.66	4		1	19		71		5
33 <i>S</i> _{1/2}	5.92	7	1	5	5	41	34	1	5
34 <i>S</i> _{1/2}	14.46	6	4		45		38	2	4
35 <i>S</i> _{1/2}	16.72	25	17	4		32	12		5

* Highest occupied molecular orbital.

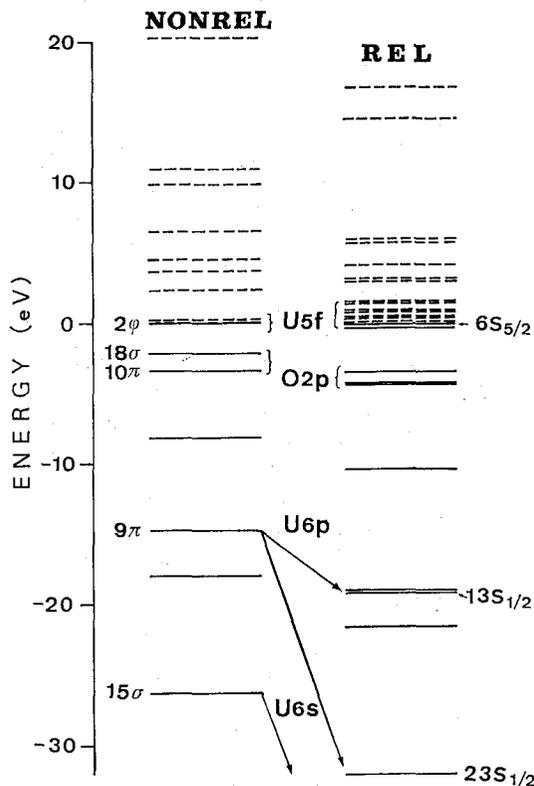


Fig. 1. Comparison of nonrelativistic and relativistic valence energy levels for UO molecule. The solid line indicates the occupied level and the dashed line represents the vacant level. The energy scale is shifted so that the energy of highest occupied level is equal to zero.

nonrelativistic and relativistic valence energy levels are shown in Fig. 1. The highest occupied molecular orbital is 2ϕ in the nonrelativistic case and $6S_{5/2}$ in the relativistic calculations. The energy scale in the figure is shifted so that the energy of these orbital corresponds to zero. The relativistic influence is clear. There is shift-down of the energy levels and the $6p$ level in the U atom is split into two levels, $6p_{1/2}$ and $6p_{3/2}$ levels, due to the spin-orbit splitting.

In conclusion, the DV- $X\alpha$ method based on the DS equation is found to be very useful to study the electronic structure of diatomic molecules with large atomic numbers. It is interesting to calculate relativistic molecular orbital correlation diagrams for heavy systems by the use of the present method.

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