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Multiple-scattered, relativistic and correlated method (MS-RCE) for molecules

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We have recently proposed a “fully” correlated relativistic local density method called RCE method [M. Vijayakumar, N. Vaidehi, and M. S. Gopinathan, *Phys. Rev. A* **40**, 6834 (1989)] for atoms and it has been shown that the results are of near Dirac–Hartree–Fock (DHF) accuracy. In this paper, the extension of the RCE method to molecules by modifying the standard multiple-scattering $X\alpha$ (MS- $X\alpha$) method is presented. Then, the modified method is applied to calculate various molecular properties such as the molecular correlation energy, the molecular orbital energy levels, the molecular orbital ionization energies, expectation value of $1/r$, and magnetic property like isotropic shielding constant for atoms in molecules. Such calculations are made for several molecules including some of them containing heavy atoms. The calculated molecular properties are compared with the available experimental results and with results calculated by other methods. The effects of relativistic and correlation corrections on these molecular properties are discussed.

I. INTRODUCTION

Many methods to perform molecular structure calculations have been reported in literature. The traditional one is the nonrelativistic *ab initio* Hartree–Fock (HF) method^{1,2} which has been successfully applied to molecules containing light atoms. The nonrelativistic HF theory does not take care of either relativistic effects or correlation. Several versions of the relativistic methods,^{3–8} the correlated methods,^{2,6,9,10} and the relativistic and correlated methods⁶ are available for atoms and molecules with different levels of computational difficulties. The most rigorous relativistic method is the Dirac–Fock (DF) method.^{3,4} Dirac–Fock one-center expansion method for molecules proposed by Mackrodt⁵ is extensively applied to study the electronic structure of metal hydrides MH_n .⁵

Using the relativistic effective core potential, complete-active-space self-consistent-field (CASSCF) method⁶ has been developed for molecules, and this method has been extensively used to study the bond properties and electronic structure of metal clusters containing heavy atoms. This method takes care of both relativistic and correlation corrections. The applications of this method has been recently reviewed by Balasubramanian.⁷ In the Dirac–Slater discrete variational (DS-DV) method,⁸ the exchange potential in the DF method is replaced by the Slater’s local exchange potential. The *ab initio* methods discussed earlier are computationally expensive and practically impossible for fairly large molecules containing many heavy atoms. To overcome the computational difficulties, semiempirical methods^{11–15} such as extended Hückel theory (EHT),¹¹ relativistic extended Hückel theory (REX),¹² complete neglect of differential overlap (CNDO) method,¹³ and the relativistic extension of the CNDO method proposed by Boca¹⁴ have been developed.

Another simple and promising approach to the molecular structure calculations is the local density methods. Many local density methods are reported in literature.^{17–22}

The density functional theory (DFT)¹⁶ with the different exchange-correlation functionals developed for atoms^{17–22} has been extended to molecules. The relativistic extension of the DFT was developed in 1973 by Rajagopal and developed by others.²² These methods have been successfully applied to calculate various molecular properties. The application of many such methods to molecules has been recently reviewed by Carrol *et al.*²³

Following the work of Slater for solids,²⁴ Johnson has developed a theory for molecules, called the multiple-scattering (MS) or scattered-wave (SW)- $X\alpha$ method or briefly MS- $X\alpha$ method.^{25–27} Because of the simplicity of the method and the rapid convergence, the MS- $X\alpha$ method has been now successfully applied to study the electronic structure of metal clusters and bonding in the transition metal complexes. The modification of the MS- $X\alpha$ method is discussed in Sec. II and results computed from the modified method are discussed in Sec. III.

II. MODIFICATION OF THE MS- $X\alpha$ METHOD: THE MS-RCE METHOD

The central idea in the MS- $X\alpha$ method is to partition the molecular space into different regions such as (i) atomic region (I), (ii) interatomic region (II), and (iii) outersphere or extramolecular region (III), and then to solve the Schrödinger equations in each region employing the appropriate boundary conditions. The computational simplicity of the MS- $X\alpha$ method is through the use of the Slater’s local exchange potential $V_1^{x\alpha}(r)$ defined as

$$V_1^{x\alpha}(r) = -6\alpha \left[\frac{3}{4\pi} \rho_1(r) \right]^{1/3}, \quad (1)$$

where α is an adjustable parameter and $\rho_1(r)$ is the sum of electron densities of all up-spin electrons of the atom “A” given by

$$\rho_{\uparrow}(r) = \sum_i n_i u_i^*(r) u_i(r). \quad (2)$$

The values of the parameter α obtained by Schwarz²⁸ ranging from 0.978 for H to 0.692 for Rn have been used in the MS-X α method.

The MS-X α package written by Cook and Case^{29,30} is converted on IBM PC/AT compatible systems by the present authors. Then the PC/AT Version of the MS-X α package is further modified according to what is given in the rest of this section. Because of the computational simplicity and the applicability of the method to molecules containing heavy atoms, the MS-X α method is widely used in many fields of research—chemistry,^{31–36} physics,^{37–40} and biology.⁴¹

The question whether the X α theory has intrinsic accuracy to warrant the inclusion of relativistic effects is an important one. However, it is difficult to decide this question *a priori* since X α method, being an approximate theory, performs differently for different properties.⁴² Relativistic extensions of semiempirical theories such as EHT^{11,12} and CNDO^{13,14} are often undertaken in the hope that specifically relativistic effects would be qualitatively described even though such theories may not have a high degree of intrinsic accuracy. It is in this spirit that the present modification of the MS-X α method is undertaken.

We now present the modification of the MS-X α method. Before proceeding further, the work on the atomic calculations is first recalled. A parameter-free self-interaction-corrected local-density method called Ξ method⁴³ has been proposed earlier for atoms. The results of the Ξ method were shown to be of near Hartree-Fock accuracy. The Ξ method was then modified further by incorporating the major relativistic correction terms in the one-electron Hamiltonian and by including the explicit expression for Coulomb correlation potential in the Hamiltonian. The results of the modified method for atoms called the relativistic and correlated Ξ or briefly RCE method⁴⁴ were shown to be of near Dirac-Hartree-Fock accuracy. The correlation energy obtained from the RCE method is in good agreement with “exact” correlation energy reported in literature and with those calculated by other methods. The atomic properties calculated by using the RCE method are in general in agreement with experimental results. Recently, the RCE method is successfully applied to calculate the Auger transition energy for light and heavy atoms.⁴⁴ Encouraged by the results of the RCE method, we extended the formalism to molecular calculations.

The average potentials used to solve the Schrödinger equation in the atomic, interatomic and outer sphere molecular regions are modified in the following way:

(i) Self-interaction corrected local exchange potential. As in the case for atoms,^{43,44} the exchange potential used to solve the Schrödinger equation in each region, is separated into self-interaction potential $V_{\uparrow}^{\text{si}}(r)$ and “pure” exchange potential $V_{\uparrow}^{\text{ex}}(r)$, as

$$V_{\uparrow}^{\text{x}}(r) = V_{\uparrow}^{\text{si}}(r) + V_{\uparrow}^{\text{ex}}(r), \quad (3)$$

where $V_{\uparrow}^{\text{si}}(r)$, the self-interaction potential at point r , is given by

$$V_{\uparrow}^{\text{si}}(r) = - \sum_i \frac{n_i u_i^*(r) u_i(r) \int n_i u_i^*(r') u_i(r') g_{rr'} dr'}{\rho_{\uparrow}(r)} \quad (4)$$

with

$$g_{rr'} = 2/|r-r'|$$

and pure exchange potential at point r , $V_{\uparrow}^{\text{ex}}(r)$, for up spin electrons derived by Vaidehi and Gopinathan,⁴³ is given as

$$V_{\uparrow}^{\text{ex}}(r) = -4\pi^{1/3} (2^{1/3} - 1) \left(\frac{1}{n} + \frac{1}{3} \right)^{-2/3} \times \sum_i \frac{\rho'_{i\uparrow}(r) \rho_{\uparrow}^{-2/3}(r) n_i u_i^*(r) u_i(r)}{\rho_{\uparrow}(r)} \quad (5)$$

and similar expressions for down spin electrons. In Eq. (5) $\rho'_{i\uparrow}(r)$ represents the density of electrons of up spin at point r excluding the density of the up spin electron in the spin-orbital $u_i(r)$

$$\rho'_{i\uparrow}(r) = \sum_{k(\neq i)\uparrow} n_k u_k^*(r) u_k(r). \quad (6)$$

Since the MS-X α method does not involve the calculation of wave functions of individual orbitals, the orbital dependent $V_{\uparrow}^{\text{si}}(r)$ and $V_{\uparrow}^{\text{ex}}(r)$ potentials are averaged out as follows.

We now define the density of the i th orbital as the average

$$\rho_{i\uparrow}(r) = \rho_{\uparrow}(r) / n_{\uparrow} \quad (7)$$

and hence $\rho'_{i\uparrow}(r)$ given in Eq. (6) becomes

$$\rho'_{i\uparrow}(r) = \rho_{\uparrow}(r) - \rho_{i\uparrow}(r) / n_{\uparrow}. \quad (8)$$

Upon substituting these expressions Eqs. (7) and (8) in Eqs. (4) and (5), we get the following expressions for $V_{\uparrow}^{\text{si}}(r)$ and $V_{\uparrow}^{\text{ex}}(r)$ potentials:

$$V_{\uparrow}^{\text{si}}(r) = -\frac{1}{n_{\uparrow}} \int dr' \rho_{\uparrow}(r') g_{rr'} \quad (9)$$

and

$$V_{\uparrow}^{\text{ex}}(r) = -\frac{4}{\pi^{1/3}} \frac{(2^{1/3} - 1) 3^{7/3}}{(2^3 - 2^{8/3})} a_{\uparrow} \left(\frac{n_{\uparrow} - 1}{n_{\uparrow}} \right) \rho_{\uparrow}^{1/3}(r), \quad (10)$$

where a_{\uparrow} is defined as⁴³

$$a_{\uparrow} = \pi^{2/3} (2^3 - 2^{8/3}) 3^{-7/3} \left(\frac{1}{n_{\uparrow}} + \frac{1}{3} \right)^{-2/3}. \quad (11)$$

Instead of the fitted parameter α used in the MS-X α method, we have used the theoretical parameter a_{\uparrow} value for the calculation of $V_{\uparrow}^{\text{ex}}(r)$ potential.

(ii) Coulomb correlation potential. We now extend the method of calculating the Coulomb correlation potential for atoms, described in Ref. 44, to molecules. In the standard MS-X α method, the Coulomb correlation is not explicitly incorporated. We use the correlation potential, in

the molecular calculations. With correlation, the final form of the average potential to be solved in each region is given as

$$V_I(r) = V^C(r) + V_{\uparrow}^{\text{si}}(r) + V_{\uparrow}^{\text{ex}}(r) + V_{\uparrow}^{\text{corr}}(r). \quad (12)$$

Here $V_{\uparrow}^{\text{corr}}(r)$ represents the average correlation potential defined as

$$V_{\uparrow}^{\text{corr}}(r) = -8/27x^3 \left[\pi \left(\frac{1}{n_{\uparrow}} + \frac{1}{3} \right) \rho_{\uparrow}(r) \right]^{-1} \\ \times \left\{ x \left[\pi \left(\frac{1}{n_{\uparrow}} + \frac{1}{3} \right) \rho_{\uparrow}(r) \right]^{-1/3} + 1 \right\}^{-1} \rho_{\uparrow}(r), \quad (13)$$

with the parameter $x=0.75$ as in atoms.

Using the modified average potential of Eq. (12), the one-electron Schrödinger equation is solved in the region I which is similar to the MS-X α method. In the intersphere region, the constant potential \bar{V}_{II} used to solve the Schrödinger equation is obtained by averaging the $V^C(r)$, $V_{\uparrow}^{\text{si}}(r)$, $V_{\uparrow}^{\text{ex}}(r)$, and $V_{\uparrow}^{\text{corr}}(r)$ over that region.

(iii) Relativistic effective core potential. As far as the relativistic corrections are concerned, in the atomic part of the modified MS-X α method, these corrections are incorporated. The relativistically corrected atomic densities are used to generate the molecular potential in the XAINPOT program.³⁰ In the molecular part, the relativistic calculations are performed by freezing the core levels of molecule. The calculation is not a full relativistic calculation in the sense that the relativistic correction terms are not incorporated in the Hamiltonian as in the case of atoms where the major relativistic correction terms are incorporated in the Hamiltonian.⁴⁴

To summarize, the present modifications of the MS-X α method are given below:

(i) Self-interaction corrected local exchange potential is used instead of the Slater's exchange potential.

(ii) Theoretical value for the parameter a is used to calculate the pure exchange potential instead of the fitted a parameter values in the MS-X α method.

(iii) The Coulomb correlation is explicitly incorporated in the molecular calculations.

(iv) The relativistic corrections are incorporated in the atomic part of the calculations and are retained in the molecular calculations by freezing the core levels.

The modified MS-X α method, called the MS-RCE method is used to calculate many molecular properties and the results are compared with the available experimental results and with the results by other methods. The present MS-RCE calculations should be regarded as preliminary or exploratory in nature designed to study the effect of the modifications discussed above.

III. RESULTS OF THE MS-RCE METHOD

In this section, the application MS-RCE method to calculate various molecular properties using the Norman

TABLE I. The Norman sphere radii^a (Bohr) used in the present calculations.^b

Molecule/Atom	Norman radius	Molecule/Atom	Norman radius
BH	B	HBr	H
	H		Br
CH	Outer	HI	Outer
	C		H
	H		I
NH	Outer	Cl ₂	Outer
	N		Cl
	H		Outer
OH	Outer	Br ₂	Br
	O		Outer
	H		
FH	Outer	I ₂	I
	F		Outer
	H		
BO	Outer	Cu ₂	Cu
	B		Outer
	O		
NO	Outer	Ag ₂	Ag
	N		Outer
	O		
B ₂	Outer	Au ₂	Au
	B		Outer
C ₂	Outer	MnO ₄ ⁻	Mn
	C		Outer
N ₂	Outer	C ₆ H ₆	O
	N		Outer
O ₂	Outer	C	H
	O		Outer
F ₂	Outer	H	Outer
	F		
H ₂ O	Outer	O	
	H		
O ₃	Outer	O	
	O		
SO ₂	Outer	S	
	S		
SF ₆	Outer	S	
	F		
HCl	Outer	F	
	H		
	Outer	Cl	
	Cl		
	Outer		

^aJ. G. Norman, Jr., Mol. Phys. 31, 1191 (1976).

^bThe experimental bond length and bond angle used are taken from CRC Handbook of Chemistry and Physics, 68th ed., 1987–1988 (CRC, Florida, 1987).

sphere radii for atoms generated by the XAINPOT program given in Table I and the results are discussed in this section.

A. Molecular correlation energy

Using the following expression, the molecular correlation is calculated in the MS-RCE method:

$$E_{\text{Present}}^{\text{corr}} = \sum_A E_A^{\text{corr}}, \quad (14)$$

where E_A^{corr} , the correlation energy of the electrons in the atomic region A , is given as

TABLE II. Molecular correlation energy (in Ry) calculated by the present MS-RCE method.

Molecule	$-E_{\text{VWN}}^{\text{corr a}}$	$-E_{\text{SPP}}^{\text{corr b}}$	$-E_{\text{GCP}}^{\text{corr c}}$	$-E_{\text{Present}}^{\text{corr d}}$	$-E_{\text{Exact}}^{\text{corr e}}$
BH	0.700	0.362	0.324	0.202	0.304
CH	0.848	0.434	0.414	0.275	0.392
NH	0.998	0.498	0.498	0.363	0.478
OH	1.208	0.620	0.630	0.455	0.620
FH	1.408	0.728	0.748	0.558	0.754
BO	1.722	0.880	0.878	0.639	0.932
NO	2.058	1.062	1.092	0.786	1.210
B ₂	1.182	0.600	0.562	0.375	0.652
C ₂	1.538	0.796	0.790	0.520	1.020
N ₂	1.890	0.978	1.000	0.696	1.090
O ₂	2.220	1.140	1.178	0.867	1.294
F ₂	2.602	1.346	1.372	1.082	1.470
H ₂ O	1.328	0.688	0.730	0.473	0.734
O ₃				1.323	
S ₂				2.476	
SO ₂				2.107	
SF ₆				4.426	
HCl				1.384	
HBr				3.696	
HI				6.162	
Cl ₂				2.704	
Br ₂				7.411	
I ₂				12.303	
Cu ₂				5.858	
Ag ₂				10.732	
Au ₂				20.412	
MnO ₄ ⁻				4.225	
C ₆ H ₆				1.764	

^aThe molecular correlation energy calculated by Vosko *et al.* taken from Ref. 23.

^bThe molecular correlation energy calculated by using the method developed by Savin *et al.* taken from Ref. 23.

^cThe gradient-corrected molecular correlation energy calculated by the method proposed by Perdew taken from Ref. 23.

^dThe molecular correlation energy calculated by using the present MS-RCE method.

^eThe exact molecular correlation energy reported by Carrol *et al.*, Ref. 23.

$$E_A^{\text{corr}} = 1/2 \int V_{A\uparrow}^{\text{corr}}(r) \rho_{\uparrow}^A(r) + 1/2 \int V_{A\downarrow}^{\text{corr}}(r) \rho_{\downarrow}^A(r), \quad (15)$$

where $V_{A\uparrow}^{\text{corr}}(r)$ is defined as in Eq. (13) and a similar expression for $V_{A\downarrow}^{\text{corr}}(r)$. The index A represents the atomic region I; and for outer sphere it represents the outer sphere region III. The summation goes over all the atoms in the molecule including the outer sphere region. In the intersphere region II, the correlation potential is calculated from the constant charge density and instead of integrating over the space, the correlation energy is calculated by multiplying the correlation potential with the total charge in that region II.

Using Eq. (14), we have calculated the molecular correlation energy for various diatomic and poly atomic molecules, some of them containing heavy atoms. In Table II, we have given the values for various diatomic molecules along with the reported results by other methods such as those proposed by Vosko *et al.* (VWN),¹⁷ Stoll *et al.* (SPP),¹⁸ and Perdew (GCP).²⁰ The "exact" molecular correlation energy²³ is also shown. From this table and Fig. 1 it is seen that correlation energy calculated by the present

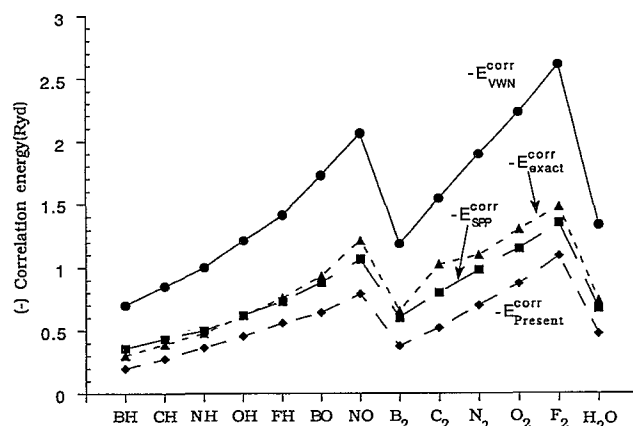


FIG. 1. Comparison of molecular correlation energy calculated by the present MS-RCE method with the exact correlation and that by other methods.

MS-RCE method is better than the VWN results but compared to SPP and GCP results, it gives slightly poorer results and the correlation energy is underestimated by the present method. One can, however, get better results by suitably adjusting the value of the parameter x used to calculate the correlation potential defined in Eq. (13). For instance, the molecular correlation energies of the molecule F_2 calculated with different values of $x=0.75$, $x=0.80$, and $x=0.85$ are 1.082, 1.280, and 1.498, respectively. From these values, it is seen that the correlation energy calculated with the parameter value $x=0.85$ is close to the exact correlation energy. This result is in agreement with the observation⁴⁴ that for the light atoms of the 1st row, the value of x should be greater than 0.75 to reproduce the exact correlation energy.

In Table II, we have also shown the correlation energy for polyatomic molecules, some of them containing heavy atoms, for which the exact correlation energy are not yet available.

B. Molecular orbital energy levels

Though eigenvalues in the Hartree-Fock theory and the $X\alpha$ theory have different physical meaning, it is instructive to compare them for different molecules. In the history of molecular quantum mechanical calculations, one of the well studied molecules is MnO_4 . We have also studied the electronic structure of this molecule. In Table III we have shown the energy levels calculated by the present MS-RCE method along with those by the MS- $X\alpha$ method²⁶ and the *ab initio* (SCFMO CI) method.⁴⁵ The valence orbitals calculated using the present method are more negative compared to the MS- $X\alpha$ or *ab initio* results while for the core orbitals, the MS-RCE method values are less negative. This is probably due to the approximation that gives the same average self-interaction and exchange potentials for core and valence levels.

TABLE III. Comparison of molecular orbital energy levels (in Ry) of MnO_4^- calculated by the present MS-RCE method with that by MS-X α and *ab initio* methods.

MO	MS-X α^a	MS-RCE ^b	<i>Ab initio</i> ^c
7a ₁	-0.006	-0.238	0.954
7t ₁	-0.350	-0.631	0.578
2e	-0.526	-0.798	0.453
1t ₁	-0.682	-0.976	-0.411
6t ₂	-0.761	-1.027	-0.487
6a ₁	-0.775	-1.187	-0.535
1e	-0.901	-1.187	-0.837
5t ₂	-0.915	-1.353	-0.876
4t ₂	-1.785	-1.734	
5a ₁	-1.813	-1.761	
3t ₂	-4.259	-4.162	
4a ₁	-6.435	-6.326	
2t (O _{1s})	-37.738	-37.612	
3a (O _{1s})	-37.738	-37.612	
1t ₂ (Mn _{2p})	-46.513	-46.574	
2a ₁ (Mn _{2s})	-54.105	-54.158	
1a ₁ (Mn _{1s})	-468.584	-468.500	

^aThe values calculated using the standard MS-X α method are taken from Ref. 26.

^bThe values are calculated by using the present MS-RCE method, but essentially without relativistic correction (i.e., without freezing the core orbitals) for comparison with MS-X α and *ab initio* results.

^cThe values calculated using the *ab initio* (SCFMO CI) method are taken from Ref. 45.

C. Ionization energy of molecular orbitals

Another well studied molecule is SF₆. We have also calculated the ionization energies of molecular orbitals (MO's) of SF₆ and the results are shown in Table IV. Using the Slater's transition state approach, the MS-X α values were calculated by Johnson.²⁶ In the calculations like X α method, transition state procedure is used to correct for the self energy of the electron.⁵³ Since we have

TABLE IV. Comparison of ionization energy (in eV) of molecular orbitals of SF₆ molecule calculated by the present MS-RCE method with those by other methods.

MO	MS-X α^a	<i>Ab initio</i> ^b	CNDO ^c	MS-RCE ^d	Expt. ^e
t _{1g}	15.9	18.2	22.4	18.2	≈16.0
t _{1u}	16.8	19.0	21.5	18.9	17.4
t _{2u}	16.8	19.4	23.1	18.8	17.3
e _g	17.5	19.4	17.8	20.9	18.7
t _{2g}	18.8	22.2	24.2	20.0	19.9
t _{1u}	21.8	24.7	29.0	23.9	22.9
a _{1g}	26.7	29.6	30.8	28.6	27.0
e _g	35.6	45.6	43.1	37.6	39.3
t _{1u}	36.5	46.8	50.8	38.5	41.2
a _{1g}	39.3	50.4	57.0	41.1	44.2

^aThe values calculated by the standard MS-X α method using the transition state procedure are taken from Ref. 26.

^bThe values calculated by the *ab initio* (IBMOL HF) method using the Δ SCF procedure are taken from Ref. 26.

^cThe ionization energies calculated by the semiempirical using the Δ SCF procedure method are taken from Ref. 26.

^dThe eigenvalues of the MS-RCE method.

^eThe experimental values are taken from Ref. 26.

TABLE V. Comparison of expectation value of $1/r$ (in a.u.) and isotropic diamagnetic shielding constant (in ppm) for the atoms in molecules calculated by the present MS-RCE method with and without relativistic corrections.

Molecule/Atom		MS-RCE			<i>Ab initio</i> ^d
		MS-X α^a	Without rel ^b	With rel ^c	
Expectation value of $1/r$					
F ₂	F:	29.93	29.88	29.87	30.04
Cl ₂	Cl:	68.95	68.70	69.63	68.88
Br ₂	Br:	184.05	183.46	187.37	183.90
I ₂	I:	320.63	319.73	334.06	319.29
Isotropic diamagnetic shielding constant					
F ₂	F:	531.23	530.39	531.02	
Cl ₂	Cl:	1223.93	1219.36	1234.54	
Br ₂	Br:	3267.04	3256.56	3325.91	
I ₂	I:	5691.32	5675.29	5929.69	

^aThe values are calculated using the MS-X α method.

^bThe values are calculated using the present MS-RCE method without relativistic corrections, i.e., without freezing the core levels in the final SCF calculations.

^cThe values are calculated with relativistic corrections by the present method.

^dThe *ab initio* (ALCHEMY program) values are taken from Ref. 52.

already included the self-interaction correction in the modified method, we have used the eigenvalues as the ionization energy to compare the experimental values. In all the following cases, we have used the eigenvalues as the ionization energy of the molecular orbitals. In general, the MS-RCE method results are in good agreement with the experimental results²⁶ and are better than that of CNDO²⁶ and MS-X α results²⁶ except for outer valence orbitals for which the present method gives high values.

D. Expectation values of $1/r$

The expectation values of the molecules F₂, Cl₂, Br₂, and I₂ are calculated using the MS-X α method and the present MS-RCE method, and the results are shown in Table V along with the *ab initio* (ALCHEMY program) results.⁵² The nonrelativistic values are obtained by using the MS-RCE method without freezing the core orbitals. In general, the nonrelativistic MS-X α and MS-RCE values agree with the *ab initio* results.⁵² The values with relativistic corrections are higher than those of nonrelativistic ones as expected. This is due to the orbital contraction of core levels of the molecule.

E. Isotropic diamagnetic shielding constant

Using the MS-X α method and the present MS-RCE method, we have calculated the isotropic diamagnetic shielding constants for some molecules with and without relativistic corrections. The results are shown in Table V. The values by MS-X α method agree with the nonrelativistic MS-RCE values. As expected, the isotropic diamagnetic shielding constant increases due to the relativistic effects.

IV. SUMMARY

In this paper, we have first discussed the modifications of the MS- $X\alpha$ method. The MS- $X\alpha$ method is modified by (1) replacing the Slater's exchange potential with the self-interaction corrected exchange potential, (2) incorporating explicitly the Coulomb correlation at the molecular level, (3) using the relativistic effective core potential and (4) using the theoretical value for the parameter a instead of the fitted value for the parameter α to calculate the exchange potential. Further, the relativistic effects are simulated by using the relativistic RCE density for the core orbitals of atoms and keeping them frozen in the molecular calculations. The modified MS- $X\alpha$ method, called "MS-RCE" method is applied to calculate various molecular properties such as correlation energy, molecular orbital energy levels, ionization energies of orbitals, expectation values of $1/r$, and magnetic properties like isotropic diamagnetic shielding constant. The results are compared with the results calculated by others methods and with the available experimental results. While the results are generally satisfactory, it appears that the "averaging approximations" need to be further improved. Also, for the accurate correlation energy calculations, one may need to use the x value for the first row atoms, which are larger than the universal value of 0.75 presently used.

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