

A Relativistic Configuration Interaction Method Using Effective Core Potentials with Spin-Orbit Interactions

Myeong Cheol Kim, Sang Yeon Lee, and Yoon Sup Lee*

Department of Chemistry and Center for Molecular Science,
Korea Advanced Institute of Science and Technology Taejeon 305-701, Korea

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As an extension to the Kramers' restricted Hartree-Fock (KRHF) method [J. Comp. Chem., 13, 595 (1992)], we have implemented the Kramers' restricted configuration interaction (KRCI) program in order to calculate excited states as well as the ground state of polyatomic molecules containing heavy atoms. This KRCI is based on determinants composed of the two-component molecular spinors which are generated from KRHF calculations. The Hamiltonian employed in the KRHF and KRCI methods contains most of all the important relativistic effects including spin-orbit terms through the use of relativistic effective core potentials (REP). The present program which is limited to a small configuration space has been tested for a few atoms and molecules. Excitation energies of the group 14 and 16 elements calculated using the present KRCI program are in good accordance with the spectroscopic data. Calculated excitation energies for many Rydberg states of K and Cs indicate that spin-orbit terms in the REP, which are derived for the ground state, are also reliable for the description of highly excited states. The electronic states of the polyatomic molecule CH_3I are probed from the molecular region to the dissociation limit. Test calculations demonstrate that the present KRCI is a useful method for the description of potential energy surface of polyatomic molecules containing heavy atoms.

Introduction

In order to achieve a good accuracy in the description of potential energy surfaces for molecules containing heavy atoms, it is necessary to include spin-orbit interactions and other relativistic effects in the electronic structure calculations.¹⁻³ Although electronic structure of molecules can be treated relativistically using ab initio all-electron method starting from the Dirac-Fock (DF) formalism,⁴⁻⁸ this approach has limited utility at present because of the large number of electrons and resulting additional integrals. Furthermore electron correlations are often essential and usually more important than the relativistic corrections. For the configuration interaction (CI) method commonly employed to account for the electron correlations, the above two factors make the all-electron relativistic calculations still more impractical.⁹

The complexity of carrying out all-electron relativistic calculations can be substantially reduced by adopting an ab initio approximate scheme known as the effective core potential methods without compromising too much accuracy. There are many variations of relativistic effective core potentials (REPs) with different generating procedures and final forms. We have been developing Hartree-Fock (HF) and post-HF methods based upon one particular form of the REP which contains spin-orbit interactions as a part of the relativistic correction. This REP was originally formulated by Lee *et al.*¹⁰ and improved by Christiansen *et al.*,¹¹ generated and tabulated in forms convenient for molecular calculations for many elements by Ermier, Christiansen and their coworkers.¹²⁻¹⁵ By defining the molecular Hamiltonian with the above REP, it is possible to include spin-orbit interactions from the HF level of the theory, but this requires modification in the computational method. We have taken this approach of including spin-orbit terms from the HF level and developed the Kramers' restricted Hartree-Fock (KRHF)¹⁶

and the MP2 method (KRMP2)¹⁷ for polyatomic molecules.

Here we report the extension to a CI method, which we will refer as the Kramers' restricted CI (KRCI) method in order to emphasize the symmetry property of the Hamiltonian used. This KRCI can be used to study excited states in addition to the ground state and has the ability to investigate open shell states of polyatomic molecules. The present KRCI method is tested for atoms and small molecules with small basis sets and configuration spaces. Theory behind the present scheme is described in the next section followed by results of some test calculations.

Theory

For a polyatomic molecule with n_v valence electrons, the two-component molecular Hamiltonian¹⁸ can be expressed (in atomic units) as

$$H = \sum_{i=1}^{n_v} \left[-\frac{1}{2} \nabla_i^2 + \sum_{a=1}^N \left(-\frac{Z_a^{\text{eff}}}{r_{ai}} + U_a^{\text{REP}} \right) \right] + \sum_{i>j}^{n_v} \frac{1}{r_{ij}} + \sum_{a>b} \frac{Z_a^{\text{eff}} Z_b^{\text{eff}}}{r_{ab}} \quad (1)$$

where i and j denote valence electrons, a and b are the core indices, Z_a^{eff} is the charge of the core a , and U_a^{REP} is the REP of atom a . There can be many variations in the form of REPs, and the present REP is expressed by the following form,^{12,16}

$$U_i^{\text{REP}} = U_{ij}^{\text{REP}}(r) + \sum_{l=0}^{L-1} \sum_{j=|l-1/2|}^{l+1/2} \sum_{m=-j}^j [U_{ij}^{\text{REP}}(r) - U_{ij}^{\text{REP}}(r)] |ljm\rangle \langle ljm| \quad (2)$$

where $|ljm\rangle \langle ljm|$ represents a two-component projection operator. Molecular spinors which are one-electron eigen-

functions of the REP of Eq. (2) have only two components while the Dirac spinors have four components. The U^{REP} of Eq. (2) can be expressed as the sum of the weighted average of REP (AREP), U^{AREP} , and the effective one-electron spin-orbit (ESO) operator, U^{SO} , as

$$U^{REP} = U^{AREP} + U^{SO} \quad (3)$$

In the above equation, the AREP has the form of

$$U^{AREP} = U_L^{AREP}(r) + \sum_{l=0}^{l-1} \sum_{m=-l}^l [U_l^{AREP}(r) - U_{l+1/2}^{AREP}(r)] |lm\rangle \langle lm| \quad (4)$$

where

$$U_l^{AREP}(r) = (2l+1)^{-1} [l \cdot U_{l-1/2}^{AREP}(r) + (l+1) \cdot U_{l+1/2}^{AREP}(r)] \quad (5)$$

and the ESO can be written as

$$U^{SO} = s \cdot \sum_{l=1}^l \frac{2}{2l+1} \Delta U_l^{REP}(r) \sum_{m=-l}^l \sum_{m'=-l}^l |lm\rangle \langle lm| 1 |lm'\rangle \langle lm'| \quad (6)$$

where

$$\Delta U_l^{REP}(r) = U_{l+1/2}^{REP}(r) - U_{l-1/2}^{REP}(r) \quad (7)$$

When the ESO is omitted in Eq. (3), the REP reduces to the AREP that is equivalent in form to many effective core potentials in the conventional nonrelativistic method. The use of the AREP in the conventional molecular orbital calculations will probably produce most relativistic effects except for the spin-orbit interactions. The spin-orbit interactions can be investigated by performing additional calculations with and without the ESO at various levels.¹⁹ In the present work, however, the spin-orbit coupling is included from the HF step to form the two-component spinors.

Even when the REP is explicitly considered, the total wavefunction of the ground state of a closed-shell system can be approximated by one Slater determinant in the HF method as

$$\Psi = \hat{A} |\psi_1 \psi_2 \cdots \psi_{n_e}| \quad (8)$$

where \hat{A} is the antisymmetrization and normalization operator and the ψ_i 's are one-electron molecular spinors with two components. In this spinor formalism, the total energy of the molecule is

$$E = \langle \Psi | H | \Psi \rangle = \sum_i^{n_e} h_i + \frac{1}{2} \sum_{ij}^{n_e} (J_{ij} - K_{ij}) + \sum_{a,b}^N \frac{Z_a^{eff} Z_b^{eff}}{r_{ab}} \quad (9)$$

where

$$J_{ij} = \langle \psi_i | J_j | \psi_i \rangle = \langle \psi_i \psi_j | \frac{1}{r_{12}} | \psi_i \psi_j \rangle \quad (10)$$

$$K_{ij} = \langle \psi_i | K_j | \psi_i \rangle = \langle \psi_i \psi_j | \frac{1}{r_{12}} | \psi_i \psi_j \rangle \quad (11)$$

All one-electron molecular spinors can be expressed as the linear combinations of the products of orbitals χ_p 's and spin functions α and β ,

$$\psi_i^+ = \sum_p c^+_{ip\alpha} \chi_p \alpha + \sum_p c^+_{ip\beta} \chi_p \beta \quad (12)$$

$$\psi_i^- = \sum_p c^-_{ip\alpha} \chi_p \alpha + \sum_p c^-_{ip\beta} \chi_p \beta \quad (13)$$

where superscripts + and - refer to Kramers' pair. With a special choice of phase factors,

$$T \psi_i^+ = -\psi_i^{-*} \quad (14)$$

$$T \psi_i^- = \psi_i^{+*} \quad (15)$$

where time reversal operator T is given by²⁰ $T = -i\sigma_y T_0$, σ_y is the Pauli matrix acting on the spin part of the spinor, and T_0 is the complex conjugation operator for the orbital part.

In the KRHF method,¹⁶ Kramers' symmetry is introduced since the two-component Hamiltonian of Eq. (1) is invariant under the operation of the time reversal symmetry. The total wave function can be written in terms of Kramers' restricted spinor pairs as

$$\Psi = \hat{A} |\psi_1 (T \psi_1) \psi_2 (T \psi_2) \cdots \psi_{n_e/2} (T \psi_{n_e/2})| \quad (16)$$

and the total electronic energy is

$$E = 2 \sum_i^{n_e/2} h_i + \sum_{ij}^{n_e/2} (2J_{ij} - K_{ij} - L_{ij}) \quad (17)$$

where

$$J_{ij} = \langle \psi_i | J_j | \psi_i \rangle = \langle \psi_i \psi_j | \frac{1}{r_{12}} | \psi_i \psi_j \rangle \quad (18)$$

$$K_{ij} = \langle \psi_i | K_j | \psi_i \rangle = \langle \psi_i \psi_j | \frac{1}{r_{12}} | \psi_i \psi_j \rangle \quad (19)$$

$$L_{ij} = \langle \psi_i | L_j | \psi_i \rangle = \langle \psi_i T \psi_j | \frac{1}{r_{12}} | T \psi_j \psi_i \rangle \quad (20)$$

By supposing linear expansions in Eq. (12) and (13) as solutions satisfying variational conditions, we obtain the Fock equation of the KRHF as

$$FC = SCE \quad (21)$$

$$F = h + \sum_i^{n_e/2} (2J_i - K_i - L_i) \quad (22)$$

where

$$J_i = \langle \psi_i | \frac{1}{r_{12}} | \psi_i \rangle \quad (23)$$

$$K_i = |\psi_i\rangle \langle \psi_i | \frac{1}{r_{12}} \langle \psi_i | \quad (24)$$

$$L_i = |T \psi_i\rangle \langle \psi_i | \frac{1}{r_{12}} \langle T \psi_i | \quad (25)$$

The appearance of the L_i is the main difference from the conventional Fock matrix. When Eq. (21) is solved, we have an orthonormal set of molecular spinors which are the linear combinations of the products of orbital bases and spin functions as in Eq. (12) and (13). Since each coefficient of ψ_i 's is a complex number in the KRHF method, each molecular spinor is also a complex function.

After molecular spinors are formed in the HF step, the transformation from the basis integrals to the molecular spinor integrals is performed using the transformation routine developed for the KRMP2 method¹⁷. The present KRCI is similar to the nonrelativistic CI in the formalism but the actual program could not be the same. Since this KRCI uses

the complex-valued integrals over molecular spinors of the KRHF, KRCI calculations require much more time and memory than the corresponding conventional CI calculations using the same REPs. The computational requirement is somewhat reduced by the utilization of the Kramers' symmetry while the treatment of complex numbers cannot be avoided in general.

If the HF wave function $|\Psi_0\rangle$ is a reasonable approximation to the exact wave function, a CI wave function $|\Phi_0\rangle$ is usually expressed as

$$|\Phi_0\rangle = C_0|\Psi_0\rangle + \sum_{aT} C_a^T|\Psi_a^T\rangle + \sum_{a<b, r<s} C_{ab}^{rs}|\Psi_{ab}^{rs}\rangle + \sum_{a<b<c, r<s<t} C_{abc}^{rst}|\Psi_{abc}^{rst}\rangle + \sum_{a<b<c<d, r<s<t<u} C_{abcd}^{rstu}|\Psi_{abcd}^{rstu}\rangle + \dots \quad (26)$$

where $|\Psi_0\rangle$, $|\Psi_a^T\rangle$, $|\Psi_{ab}^{rs}\rangle$, ... denote determinants. In our KRCI, all the determinants are orthogonal to each other because the spinors composing them constitute an orthonormal set. If the normalization is imposed, the linear variation method leads to an eigenvalue equation,

$$HC = CE \quad (27)$$

where the element of the Hamiltonian matrix, H ,

$$H_{ij} = \langle \Psi_i | H | \Psi_j \rangle. \quad (28)$$

The expression of each matrix element H_{ij} is derived from the Slater-Condon rules. Integrals over molecular spinors can be grouped as one- and two-electron integrals.

$$[i|h|j] = \int dx_1 \psi_i^*(x_1) h(x_1) \psi_j(x_1) \quad (29)$$

$$[ij|kl] = \int dx_1 dx_2 \psi_i^*(x_1) \psi_j(x_1) r_{12}^{-1} \psi_k^*(x_2) \psi_l(x_2). \quad (30)$$

For the orbital integrals which are used to form nonrelativistic C_i matrix, one can take advantage of the following symmetries,

$$[i|h|j] = [j|h|i] \quad (31)$$

$$[ij|kl] = [ji|kl] = [ij|lk] = [ji|lk] \\ = [kl|ij] = [kl|ji] = [lk|ij] = [lk|ji] \quad (32)$$

because all integrals are real numbers. In the present method, it is necessary to consider complex conjugation whenever permutation is used to reduce the number of integrals to be explicitly evaluated, *i.e.* Eq. (31) changes to $[i|h|j] = [j|h|i]^*$ and the symmetries in Eq. (32) are partially broken because the spinors are complex vectors. For the molecular spinor integrals, only the Hermitian symmetry exists,

$$[ij|kl] = [kl|ij] = [ji|lk]^* = [lk|ji]^* \quad (33)$$

$$[ji|kl] = [kl|ji] = [ij|lk]^* = [lk|ij]^* \quad (34)$$

In the present KRCI method, the Kramers' symmetry compensates for the lowered symmetry with the following relationships²⁰,

$$[ji|kl] = [ij|TkTl]^* \quad (35)$$

$$[iTj|kl] = -[Tij|TkTl]^* \quad (36)$$

Table 1. Excitation Energies of Some Group 14 Elements in cm^{-1}

Term.	Ge		Sn		Pb	
	Exp.	KRCI	Exp.	KRCI	Exp.	KRCI
³ P $J=0$	0.0	0.0	0.0	0.0	0.0	0.0
$J=1$	557.1	552.3	1691.8	1742.1	7819.4	7467.6
$J=2$	1409.9	1409.4	3427.7	3654.4	10650.5	11240.9
¹ D $J=2$	7125.3	9827.5	8613.0	11228.2	21457.9	22163.2
¹ S $J=0$	16367.2	17442.2	17162.6	18409.1	29466.8	30657.3

where $T(Tj) = -j$.

To solve Eq. (27) is to diagonalize the matrix H . We have coded a simple CI routine that constructs the H matrix by comparing determinants. The diagonalization of the complex Hermitian matrix is performed by using the EVCHF routine from the IMSL library²¹ to get the eigenvectors and the corresponding eigenvalues.

Test Calculations and Results

Seven different computational methods, four based upon the use of AREP and three of REP, are used in this study. The relativistic restricted HF using the AREP (AREP-HF) is the HF method including all the relativistic effects except the spin-orbit coupling. Solutions obtained from the AREP-HF are called molecular orbitals in this work because of the lack of spin-orbit coupling. The relativistic Möller-Plesset second order perturbation using the solutions of the AREP-HF (AREP-MP2) calculates the perturbation energy with molecular orbital integrals. The relativistic CI using the solutions of the AREP-HF (AREP-CI) is a CI approach using the same molecular orbital integrals as the AREP-MP2 while the addition of spin-orbit integrals in forming the CI matrix will lead to the spin-orbit CI method, which will be referred as AREP-SOCI. There are three REP methods, REP-KRHF, REP-KRMP2, and REP-KRCI. They are based on two-component molecular Hamiltonian and take advantage of Kramers' symmetry. REP-KRHF produces two-component molecular spinors and REP-KRMP2 calculates the second order perturbation energy using the molecular spinor integrals. REP-KRCI calculates CI energies using integrals over molecular spinors.

Full CI calculations with the REPs and minimal basis sets¹³⁻¹⁵ were performed for group 14 elements Ge, Sn, and Pb and group 16 elements Se, Te, and Po. Since the full CI calculation was performed for each element, AREP-SOCI and REP-KRCI gave the identical excitation energies. This provides one crucial check for the correctness of our implementation of the KRCI computer code. Tables 1 and 2 show that excitation energies from these crude calculations are accurate to 75-95% in comparison with the experimental spectroscopic data.²² Large $\Delta E(^3P_1-^3P_0)$ and $\Delta E(^1D_2-^3P_2)$ of Pb which are expected for the heaviest element of the group 14 demonstrate the need to include spin-orbit interactions even for the qualitatively correct results. Large $\Delta E(^3P_1-^3P_2)$, negative $\Delta E(^3P_0-^3P_1)$, and large $\Delta E(^1S_0-^1D_2)$ of Po are also

Table 2. Excitation Energies of Some Group 16 Elements in cm^{-1}

Term.	Ge		Te		Po	
	Exp.	KRCI	Exp.	KRCI	Exp.	KRCI
$^3\text{P } j=2$	0.0	0.0	0.0	0.0	0.0	0.0
$j=1$	1989.5	2125.2	4751.	4874.1	16831.	16942.3
$j=0$	2534.4	2723.2	4407.	4923.6	7514.	8383.8
$^1\text{D } j=2$	9576.1	12379.4	10559.	13336.9	21679.	24074.2
$^1\text{S } j=0$	22446.0	22612.7	23199.	23585.3	42718.	44924.5

reproduced by the present KRCI scheme. Nonrelativistic *ab initio* calculations do not produce splittings of ^3P unless the spin-orbit interactions are added. It is impossible for the nonrelativistic CI to calculate the above ΔE 's.

Rydberg states of K and Cs atoms were calculated using the REPs^{13,15} and moderate basis sets including some Rydberg exponents (total of 11s11p basis functions and no contractions) at the CI level of single electron excitation. Determinants were constructed by using the molecular spinors

from the REP-KRHF calculations of the positive ion. Excitation energies of K are listed in Table 3 and those of Cs are in Table 4. The excitation energies of REP-KRCI and AREP-KRCI are about the same and systematically smaller than the experimental values²² indicating that low-lying states are not described very well by the present scheme. Spin-orbit splittings are calculated better by the REP-KRCI than by the AREP-SOCI method implying that the REP-KRCI may be superior to the AREP-SOCI method for this type of properties. Improvements of excitation energies and spin-orbit splittings are expected for more elaborate CI schemes. Relative errors in spin-orbit splittings are rather uniform regardless of n quantum numbers except for the very last states. This is a good indication that the ESO contained in the REP is good not only for the ground states, for which ESO was derived, but also for highly excited states.

Figure 1 shows the six different dissociation curves for the ground state of the HBr which are calculated using the REP¹² and the double zeta basis sets for Br and H. Due to the limitations in the HF theory, AREP-HF, AREP-MP2, REP-KRHF, and REP-KRMP2 can not dissociate the HBr into H and Br atoms. Two CI calculations, AREP-SOCI and

Table 3. Excitation Energies (in cm^{-1}) for Rydberg States $^2\text{P}_{1/2}$ and $^2\text{P}_{3/2}$ of the K atom

Config.	Term	Exp.	REP-KRCI	Error ^a	AREP-SOCI	Error ^a
$3p^5 4p^1$	$^2\text{P}_{1/2}$	12985.17	11347.8		11353.5	
	$^2\text{P}_{3/2}$	13042.89	11394.6		11391.5	
	$\Delta E(^2\text{P}_{3/2} - ^2\text{P}_{1/2})$	57.72	46.8	-18.9%	38.0	-34.2%
$3p^5 5p^1$	$^2\text{P}_{1/2}$	24701.44	22349.9		22351.7	
	$^2\text{P}_{3/2}$	24720.20	22365.9		22364.8	
	$\Delta E(^2\text{P}_{3/2} - ^2\text{P}_{1/2})$	18.76	16.0	-14.7%	13.1	-30.2%
$3p^5 6p^1$	$^2\text{P}_{1/2}$	28999.29	26498.2		26498.9	
	$^2\text{P}_{3/2}$	29007.70	26505.2		26504.6	
	$\Delta E(^2\text{P}_{3/2} - ^2\text{P}_{1/2})$	8.41	7.0	-16.7%	5.7	-32.2%
$3p^5 7p^1$	$^2\text{P}_{1/2}$	31069.98	28572.5		28572.7	
	$^2\text{P}_{3/2}$	31074.46	28575.4		28575.1	
	$\Delta E(^2\text{P}_{3/2} - ^2\text{P}_{1/2})$	4.48	2.9	-35.3%	2.4	-46.4%

^aDifference between experimental and calculated ΔE .

Table 4. Excitation Energies (in cm^{-1}) for Rydberg States $^2\text{P}_{1/2}$ and $^2\text{P}_{3/2}$ of the Cs atom

Config.	Term	Exp.	REP-KRCI	Error ^a	AREP-SOCI	Error ^a
$5p^5 6p^1$	$^2\text{P}_{1/2}$	11178.24	9131.3		9147.2	
	$^2\text{P}_{3/2}$	11732.35	9526.4		9487.4	
	$\Delta E(^2\text{P}_{3/2} - ^2\text{P}_{1/2})$	554.11	395.1	-28.7%	340.2	-38.6%
$5p^5 7p^1$	$^2\text{P}_{1/2}$	21765.65	18703.9		18699.0	
	$^2\text{P}_{3/2}$	21946.66	18845.6		18821.8	
	$\Delta E(^2\text{P}_{3/2} - ^2\text{P}_{1/2})$	181.01	141.7	-21.7%	122.8	-32.2%
$5p^5 8p^1$	$^2\text{P}_{1/2}$	25709.14	22420.4		22409.5	
	$^2\text{P}_{3/2}$	25791.78	22485.8		22466.2	
	$\Delta E(^2\text{P}_{3/2} - ^2\text{P}_{1/2})$	82.64	65.4	-20.9%	56.7	-31.4%
$5p^5 9p^1$	$^2\text{P}_{1/2}$	27637.29	24287.0		24273.4	
	$^2\text{P}_{3/2}$	27681.96	24317.9		24300.2	
	$\Delta E(^2\text{P}_{3/2} - ^2\text{P}_{1/2})$	44.67	30.9	-30.8%	26.8	-40.0%

^aDifference between experimental and calculated ΔE .

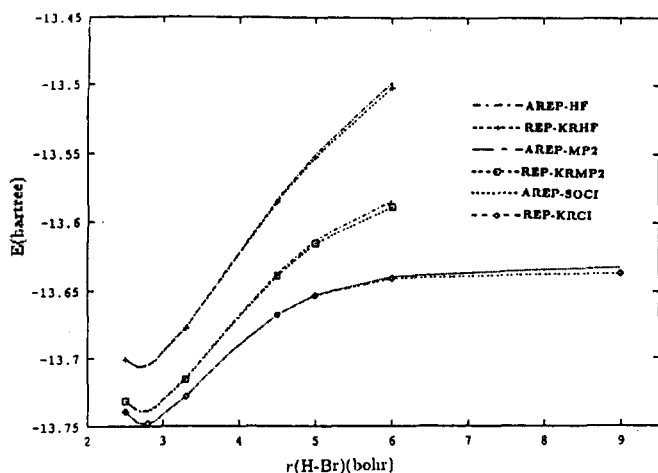


Figure 1. Potential energy curves for the ground state of BrH.

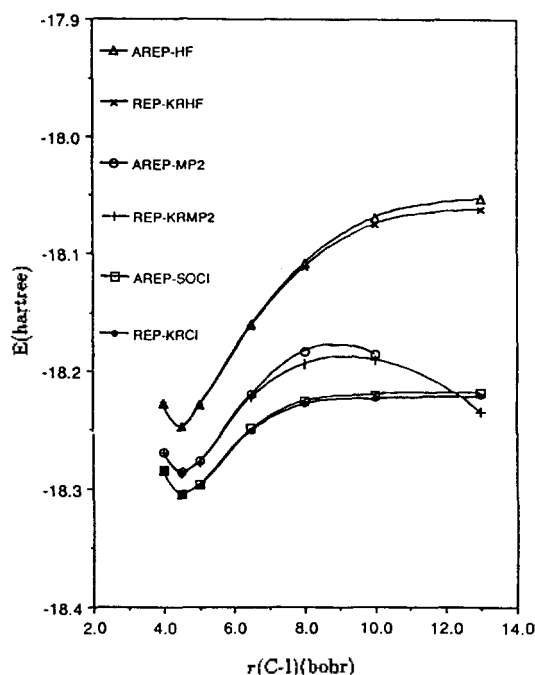


Figure 2. Potential energy curves for the ground state of CH₃I.

REP-KRCI, however, exhibit qualitative dissociations. The dissociation energy 2.99 eV of both AREP-SOCI and REP-KRCI is a reasonable value when compared with the experimental one of 3.92 eV.²³ At the molecular region near R_e , there are almost no difference between AREP and REP calculations, but more difference is found with the increase of internuclear distance reflecting the fact that the spin-orbit interactions are usually larger for the atoms than for the molecules.

Figure 2 shows six energy curves for the ground state of CH₃I. Those curves were obtained using REPs and the minimal basis sets.^{12,14} Each geometry is optimized at fixed $r(\text{C-I})$ using AREP-UHF calculations. Single and double excitations are included in these CI calculations. Two CI energy curves, AREP-SOCI and REP-KRCI, exhibit qualitatively correct dissociations, which means that our KRCI program is adequate for probing nonlinear polyatomic molecules. A few

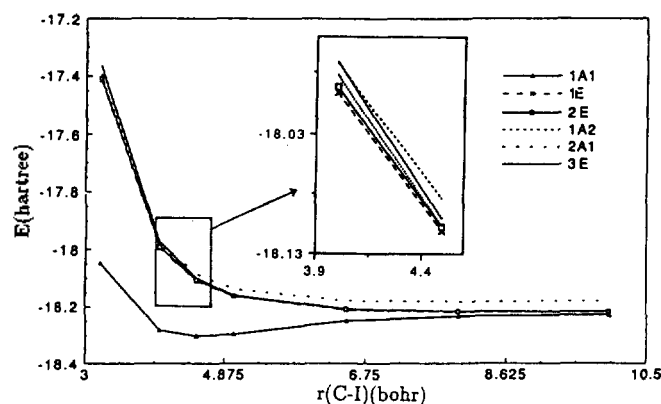


Figure 3. Potential energy curves for low-lying states of CH₃I computed using the REP-KRCI.

low-lying states were calculated by REP-KRCI in order to test the performance on excited states of the polyatomic molecules. The photoexcitation of CH₃I may follow two dissociation channels, $I(^2P_{1/2}) + \text{CH}_3$ and $I(^2P_{3/2}) + \text{CH}_3$.²⁴ Calculated energy curves of some low-lying states in Figure 3 are in good accordance with the experiment.²⁴ Even the conical cross section, the crossover between 3E and 2A₁ states is also present in the present KRCI results. As $r(\text{C-I})$ becomes long enough to be considered as the dissociated CH₃I, four excited states 3E, 1A₂, 2E, and 1E converge to the channel $I(^2P_{3/2}) + \text{CH}_3$ and the excited state 2A₁ does to the other channel $I(^2P_{1/2}) + \text{CH}_3$. The channel $I(^2P_{3/2}) + \text{CH}_3$ of 3E, 1A₂, 2E, and 1E, however, did not exactly coincide with that of 1A₁ in the dissociation limit since the present KRCI is based on the single reference state which does not possess equivalent p orbitals. The excitation energies from the ground state 1A₁ to 2E, 2A₁, and 3E are 232, 209, and 224 nm, respectively, in reasonable agreement with the experimental broad band centered around 260 nm.^{25,26}

Concluding Remarks

We have implemented the KRCI program to calculate excited states as well as the ground state of polyatomic molecules having heavy atoms. This KRCI is based on determinants composed of the products of two-component molecular spinors which are the solutions from the KRHF program and uses molecular spinor integrals with all the important one-electron relativistic effects including the spin-orbit interaction.

Excitation energies of the group 14 and 16 elements calculated using the present KRCI program are in good accordance with the spectroscopic data. Rydberg states of K and Cs were investigated. Results indicate that the REP-KRCI method is slightly better than the AREP-SOCI for the calculation of spin-orbit splittings and that ESO of REP is a reliable description of spin-orbit interactions even for the highly excited states. The KRCI scheme is able to dissociate diatomic molecule HBr properly. The electronic states of the polyatomic molecule CH₃I are probed from the molecular region to the dissociation limit. The differences between AREP-SOCI and REP-KRCI calculations are not significant and can be attributed to the difference of the reference state. Wheth-

er this will be true in general or not remains to be proved by more extensive test calculations. Any serious consideration of dynamic correlation effects requires a more efficient version of the KRCI method and the work in this direction is in progress.

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