

# Extended Koopmans' Theorem: Approximate Ionization Energies from MCSCF Wave Functions

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Received 10 January 1992; accepted 27 April 1992

The extended Koopmans' theorem has been implemented using multiconfigurational self-consistent field wave functions calculated with the GAMESS, HONDO, and SIRIUS programs. The results of illustrative calculations are presented for the molecules HF, H<sub>2</sub>O, NH<sub>3</sub>, CH<sub>4</sub>, N<sub>2</sub>, CO, HNC, HCN, C<sub>2</sub>H<sub>2</sub>, H<sub>2</sub>CO, and B<sub>2</sub>H<sub>6</sub>. The lowest extended Koopmans' theorem ionization potentials agree well within the experimental values and the ionization potentials representing excited states of the ions show some improvements over the Koopmans' theorem values in most cases. The extended Koopmans' theorem is easily implemented and the time required to calculate the ionization energies is insignificant compared to the time required to calculate the wave function of the un-ionized molecule. © 1992 by John Wiley & Sons, Inc.

## INTRODUCTION

The Koopmans' theorem<sup>1</sup> (KT) for Hartree-Fock or self-consistent field (SCF) wave functions provides us with a simple model for ionization. The electron is removed from an orbital (or equivalently the orbital is removed from the wave function) and the ionization energy is the negative of the orbital energy. The extended Koopmans' theorem (EKT)<sup>2-4</sup> combines an orbital model for ionization with a many-electron wave function. The removal of an orbital  $q(\mathbf{x}_N)$  from a reference wave function  $\Psi^N(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$  can be expressed as

$$\Psi^{N-1} = \int q(x_N) \Psi^N(x_1, \dots, x_N) dx_N \quad (1)$$

This can also be expressed as

$$|\Psi^{N-1}\rangle = \hat{q}|\Psi^N\rangle \quad (2)$$

where  $\hat{q}$  is a linear combination of annihilation operators,

$$\hat{q} = \sum_i c_i \hat{a}_i \quad (3)$$

The operator  $\hat{a}_i$  annihilates orbital  $\phi_i$  from the  $N$ -electron wave function. The ionization energy is

the energy difference between  $E^{N-1}$  and  $E^N$ ,

$$\begin{aligned} \varepsilon = E^N - E^{N-1} &= \langle \Psi^N | \hat{H} | \Psi^N \rangle - \frac{\langle \Psi^N | \hat{q}^\dagger \hat{H} \hat{q} | \Psi^N \rangle}{\langle \Psi^N | \hat{q}^\dagger \hat{q} | \Psi^N \rangle} \\ &= - \frac{\langle \Psi^N | \hat{q}^\dagger [\hat{H}, \hat{q}] | \Psi^N \rangle}{\langle \Psi^N | \hat{q}^\dagger \hat{q} | \Psi^N \rangle} \end{aligned} \quad (4)$$

Here the reference wave function must be an eigenfunction of the model Hamiltonian  $\hat{H}$ . The reference wave function could be a single determinant, a full configuration interaction (CI) wave function, a multiconfigurational self-consistent field (MCSCF) wave function, the exact wave function, or some other wave function that is an eigenfunction of a model Hamiltonian. If the reference wave function is a Hartree-Fock single determinant, then eq. (1) represents the removal of an electron from one of the canonical Hartree-Fock orbitals and the ionization energy is the negative of the orbital energy obtained from Koopmans' theorem. If the wave function contains electron correlation, then eqs. (1)–(4) represent the extended Koopmans' theorem.

For an orbital basis set of dimension  $M$  the orbital annihilation operators,  $\hat{a}_i$ , can be used to generate a set of  $M$  functions,  $\Psi_i^{N-1}$ , which in general is not complete. In fact as  $M$  increases, the size of the basis set becomes much smaller than the set of all symmetry-adapted  $(N-1)$ -electron configurations that can be formed from the  $M$  orbitals. Using the  $c_i$  of eq. (3) as variational coefficients, the or-

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bitals  $q_i(\mathbf{x})$  and orbital energies  $\varepsilon_i$  are found by solving the matrix equations

$$(\mathbf{V} - \varepsilon\gamma)\mathbf{c} = \mathbf{0} \quad (5)$$

where

$$V_{ij} = -\langle \Psi^N | \hat{a}_i^\dagger [\hat{H}, \hat{a}_j] | \Psi^N \rangle \quad (6)$$

The matrix  $\gamma$  is the overlap matrix of the  $(N-1)$ -electron functions  $\Psi_i^{N-1}$ , and is the first-order reduced density matrix,

$$\gamma_{ij} = \langle \Psi^N | \hat{a}_i^\dagger \hat{a}_j | \Psi^N \rangle \quad (7)$$

In other contexts the  $\mathbf{V}$  matrix has been referred to as a generalized Fock matrix<sup>5</sup> and as the Lagrange multipliers matrix for imposing orbital orthonormality constraints in an MCSCF variational formulation.<sup>6</sup> We refer to it as the orbital Lagrange multiplier matrix emphasizing its connection to MCSCF calculations. Some MCSCF computer codes monitor the asymmetry of the  $\mathbf{V}$  matrix as an indication of the degree of convergence of the MCSCF calculation. An MCSCF calculation has converged when the wave function becomes an eigenfunction of the second-quantized form of the Hamiltonian that is truncated to the orbital basis used in the MCSCF calculation. Convergence can also be monitored by using the gradient,<sup>7</sup> or other quantities that reflect the degree to which the MCSCF wave function has become an eigenfunction of the truncated second-quantized Hamiltonian.

The matrix  $\mathbf{V}$  can be expressed in terms of the reduced first-order and second-order reduced density matrices:

$$V_{ij} = \sum_k h_{ik} \gamma_{jk} + 2 \sum_{k,l,m} g_{iklm} \Gamma_{jklm} \quad (8)$$

where the elements of the second-order reduced density matrix are

$$\Gamma_{iklm} = \langle \Psi^N | \hat{a}_i^\dagger \hat{a}_k^\dagger \hat{a}_m \hat{a}_l | \Psi^N \rangle \quad (9)$$

and  $h_{ij}$  and  $g_{iklm}$  are integrals over the one-electron and two-electron parts of the Hamiltonian, respectively.

The extended Koopmans' theorem may be used to calculate ionization energies corresponding to orbitals that are not occupied in the single configuration wave function of the un-ionized system. For example, it would be possible to obtain ionization energies representing a transition from the  $1s^2 2s^2$  state of Be to the  $1s^2 2p$  state of  $\text{Be}^+$ , which would not be possible using Koopmans' theorem for a Hartree-Fock wave function. The annihilator for a  $2p\beta$  orbital from a CI wave function would annihilate this orbital from any configurations containing it, and would eliminate any configurations that do not contain it, leaving behind a wave function for the  $1s^2 2p\alpha$  state of  $\text{Be}^+$ .

The early calculations of the ionization poten-

tials of atoms<sup>3,8,9</sup> using the EKT indicated that good valence shell ionization potentials could be obtained and that ionization potentials representing ionization into excited states of the ion, which are not obtainable using Koopmans' theorem, could also be calculated. EKT calculations on  $F_2$ <sup>10</sup> and  $N_2$ <sup>11</sup> gave orbital energies that were in the correct order whereas the KT orbital energies are not. More recent calculations indicate that the lowest ionization potential can be obtained to arbitrary accuracy.<sup>12</sup>

In this article we discuss the implementation of the EKT using existing MCSCF computer programs and we present the results of calculations for several small molecules.

## METHOD

At least some computer packages that perform MCSCF calculations compute both the  $\mathbf{V}$  and  $\gamma$  matrices and therefore they can be easily adapted to perform extended Koopmans' theorem calculations. The diagonalization of the matrix  $\mathbf{V}$  in the metric  $\gamma$  represents a very small fraction of total computer time required for an MCSCF calculation. For example, an MCSCF calculation might require on the order of hours whereas the EKT calculation would typically require a fraction of a second. Therefore EKT calculations are essentially free after the MCSCF wave function has been obtained.

The  $\mathbf{V}$  and  $\gamma$  matrices are block diagonal with respect to  $\alpha$  and  $\beta$  spin type. For singlet states the  $\mathbf{V}_{\alpha\alpha}$  and  $\mathbf{V}_{\beta\beta}$  blocks of the Lagrange multiplier matrix are equal as are the  $\gamma_{\alpha\alpha}$  and  $\gamma_{\beta\beta}$  blocks of the density matrix. The GAMESS,<sup>13</sup> HONDO,<sup>14</sup> and SIRIUS<sup>15</sup> computer programs use the sum of the two blocks

$$\mathbf{V} = \mathbf{V}_{\alpha\alpha} + \mathbf{V}_{\beta\beta}$$

and

$$\gamma = \gamma_{\alpha\alpha} + \gamma_{\beta\beta}$$

These programs cannot be used without modification to perform EKT calculations using reference wave functions for states that are not singlet.

In the GAMESS and HONDO programs the  $\mathbf{V}$  and  $\gamma$  matrices are found on direct-access files that are maintained by internal routines. The EKT subroutines are linked and loaded with the programs and use the internal routines to access the direct-access files. The SIRIUS program provides a file for post-processing that contains the  $\mathbf{V}$  and  $\gamma$  matrices so the EKT calculation can be performed by a separate program that is run after the SIRIUS program has generated the MCSCF wave function.

The matrix equations can be solved by using

symmetric orthonormalization to get the equations

$$(\mathbf{V}' - \epsilon \mathbf{I})\mathbf{c}' = \mathbf{0} \quad (10)$$

where

$$\mathbf{V}' = \gamma^{-1/2} \mathbf{V} \gamma^{-1/2}$$

The natural transition orbitals (NTO) are given by

$$\chi_i = \sum_j c_{ji} \phi_j \quad (11)$$

and the corresponding  $\epsilon_i$  are their orbital energies. The negative of the orbital energies are approximate ionization potentials

$$I_i = -\epsilon_i$$

Numerical difficulty may arise in the above equations when the natural orbital occupation numbers become very small. In that case a canonical orthonormalization can be performed and the natural orbitals with the lowest occupation numbers eliminated. However, some of our trial calculations using this algorithm have resulted in significantly higher ionization potentials. It appears that natural orbitals that may have relatively low weight in the wave function for the un-ionized system may be required to adequately describe the ionized system.

## RESULTS

The calculations, except for  $\text{N}_2$ , were performed using the TZP or DZP basis sets from the HONDO program. These basis sets are those of Dunning and Hay<sup>16</sup> augmented by polarization functions available in the HONDO program. The TZP basis sets for B, C, N, O, and F are the 11s6p contracted to 5s3p augmented with 1 *d* orbital, and the DZP basis sets are the 10s5p contracted to 3s2p augmented with 1 *d* orbital. The TZP basis set for H is 5s contracted to 3s augmented with 1 *p* orbital and the DZP basis for H is 4s contracted to 2s with 1 *p* orbital. Starting orbitals for the MCSCF calculations were either the SCF orbitals or natural orbitals generated by a second-order Møller–Plesser perturbation calculation.

The results of EKT calculations are compared with experimental vertical ionization potentials and Greens' function (GF) calculations.<sup>17</sup> For  $\text{N}_2$  the EKT results are also compared with multiconfigurational electron propagator (MCEP)<sup>11</sup> results. The GF calculations are based on a single configuration reference using perturbation theory whereas the MCEP calculations are based on a multiconfigurational MCSCF reference wave function.

## HF

A full CI calculation was performed on HF at the equilibrium internuclear distance of 0.917 Å using

**Table I.** Ionization potentials for HF in eV.

	EKT	$\Delta$ CI	KT	Exp.
1 $\pi$	16.27	16.10	17.60	16.19 <sup>a</sup>
3 $\sigma$	20.35	—	20.82	19.9 <sup>a</sup>
2 $\sigma$	41.93	—	43.52	39.6 <sup>b</sup>

<sup>a</sup>Ref. 18.

<sup>b</sup>Ref. 19.

the TZP basis set and an orbital space of 1-6 $\sigma$  and 1-2 $\pi$  SCF orbitals. The CI wave function contains 5180 terms in  $\text{C}_{2v}$  symmetry. The SCF energy in this basis is  $-100.0601$  a.u. and the CI energy is  $-100.2066$  a.u. A full CI calculation was also carried out for the  $^2\Pi$  state of the ion. Although lower bounds to the EKT IP are not generally provided by  $\Delta$ CI calculations, a lower bound to the EKT IP can be obtained when the EKT reference wave function on the un-ionized molecule is a full CI wave function and a full CI wave function in the same basis is obtained for the ionized molecule. The  $\Delta$ CI IP obtained as the energy difference of these two full CI wave functions then provides a lower bound for the corresponding EKT IP.

Results listed in Table I are compared with KT and experimental values for the 3 $\sigma$ , 1 $\pi$ , and 2 $\sigma$  IPs and with the  $\Delta$ CI calculation. The lowest EKT ionization potential is a significant improvement over the KT value. The other EKT IPs are not much different from the KT values. The  $\Delta$ CI IP for the 1 $\pi$  orbital is slightly below the experimental value while the EKT value is slightly above it.

## H<sub>2</sub>O

Two wave functions were calculated for  $\text{H}_2\text{O}$  at  $R_{\text{O-H}} = 0.958$  Å and  $\theta_{\text{HOH}} = 104.5^\circ$  using the TZP basis set. The first,  $\Psi^I$ , was a 5072 term full CI wave function in an active space of orbitals 1-5a<sub>1</sub>, 1-2b<sub>1</sub>, and 1-3b<sub>2</sub>. The second,  $\Psi^{II}$ , was a 18,385 term complete active space (CAS) MCSCF wave function with eight electrons in an active space of orbitals 2-7a<sub>1</sub>, 1-2b<sub>1</sub>, and 1-4b<sub>2</sub>. The energies are  $E(\Psi^I) = -76.1942$  a.u. and  $E(\Psi^{II}) = -76.2210$  a.u. The SCF energy in the TZP basis is  $-76.0534$  a.u. A full CI calculation was performed on the ion using the same orbitals used for  $\Psi^I$ . Results are compared with GF calculations, Koopmans' theorem IPs, and experimental values in Table II. The lowest EKT and GF ionization potentials are comparable although they bracket the experimental value.

## NH<sub>3</sub>

Two MCSCF wave functions were calculated for  $\text{NH}_3$  at the equilibrium geometry of  $R_{\text{NH}} = 1.012$  Å and  $\theta_{\text{HNH}} = 106.7^\circ$  using the TZP basis set. The first,  $\Psi^I$ , was calculated using an active space of 1-

**Table II.** Ionization potentials for H<sub>2</sub>O in eV.

	EKT( $\Psi^I$ )	EKT( $\Psi^{II}$ )	$\Delta$ CI( $\Psi^I$ )	KT	GF <sup>a</sup>	Exp. <sup>b</sup>
1b <sub>1</sub>	12.55	12.51	12.44	13.80	12.90	12.78
3a <sub>1</sub>	14.93	15.04	—	15.59	14.85	14.83
1b <sub>2</sub>	19.48	19.50	—	19.51	18.91	18.72
2a <sub>1</sub>	35.70	35.55	—	36.79	33.41	32.61

<sup>a</sup>Ref. 20.<sup>b</sup>Refs. 21 and 22.

6a<sub>1</sub> and 1-3e, with an excitation level of 4. The second,  $\Psi^{II}$ , is a CAS MCSCF wave function with 1a<sub>1</sub> core orbital and an active space of 2-5a<sub>1</sub> and 1-3e orbitals. The wave function  $\Psi^I$  contains 12,634 configurations and  $\Psi^{II}$  has 16,542 configurations using C<sub>s</sub> symmetry. The SCF energy in the TZP basis is -56.2160 a.u. and the MCSCF energies are  $E(\Psi^I) = -56.3582$  a.u. and  $E(\Psi^{II}) = -56.3579$  a.u. The EKT ionization potentials are compared with KT, GF, and experimental values in Table III. The lowest EKT value is a significant improvement over the KT value. There are not significant differences between the EKT IPs calculated from the two wave functions.

## CH<sub>4</sub>

A full CI wave function was calculated for CH<sub>4</sub> at the equilibrium geometry,  $R_{\text{CH}} = 1.092$  Å, using the TZP basis set and an active orbital space of 1-3a<sub>1</sub> and 1-3t<sub>2</sub>. The CI wave function contains 43,194 terms in C<sub>2v</sub> symmetry. The CI energy is -40.3271 a.u. and the SCF energy in the TZP basis is -40.2095 a.u. A full CI calculation was also carried out on the <sup>2</sup>A<sub>1</sub> state of the ion in the same basis. Results are compared with GF, KT, and experimental ionization potentials in Table IV. The EKT and GF values are comparable for the lowest ionization potential, while the EKT offers only a slight improvement over the KT value for the 2a<sub>1</sub> ionization.

**Table III.** Ionization potentials for NH<sub>3</sub> in eV.

	EKT( $\Psi^I$ )	EKT( $\Psi^{II}$ )	KT	GF <sup>a</sup>	Exp.
3a <sub>1</sub>	10.69	10.69	11.60	10.72	10.8 <sup>a</sup>
1e	17.00	17.09	17.11	16.41	16.8 <sup>b</sup>
2a <sub>1</sub>	30.38	30.27	31.08	27.48	27.7 <sup>c</sup>

<sup>a</sup>Ref. 23.<sup>b</sup>Ref. 24.<sup>c</sup>Ref. 25.**Table IV.** Ionization potentials for CH<sub>4</sub> in eV.

	EKT	$\Delta$ CI	KT	GF <sup>a</sup>	Exp. <sup>a</sup>
1t <sub>2</sub>	14.60	14.18	14.81	14.05	14.40
2a <sub>1</sub>	25.51	—	25.62	23.68	23.0

<sup>a</sup>Ref. 26.

## N<sub>2</sub>

Four wave functions were used for the N<sub>2</sub> molecule. The first,  $\Psi^I$ , is an MCSCF wave function from Dunning's<sup>27</sup> 5s4p basis augmented with one *d* polarization function (basis set I). This basis set gives an SCF energy of -108.9780 a.u. The  $\Psi^I$  wave function has an excitation level of 2 and the active orbitals are 2-6 $\sigma_g$ , 2-5 $\sigma_u$ , 1-3 $\pi_u$ , and 1-2 $\pi_g$ . The MCSCF energy from this wave function is -109.2325 a.u. The second,  $\Psi^{II}$ , is a wave function from Dunning's<sup>27</sup> 4s2p augmented with a fifth *s* orbital with exponent 0.02 and a third *p* orbital with exponent 0.015 and a *d* polarization function (basis set II). This basis set gives an SCF energy of -108.9618 a.u. The active orbitals and excitation level in  $\Psi^{II}$  are the same as those for  $\Psi^I$ . The MCSCF energy from this wave function is -109.2060 a.u. The third and fourth wave functions are CAS MCSCF wave functions in the same basis used for  $\Psi^I$ . The wave functions  $\Psi^{III}$  has an active space of 2 $\sigma_u$ , 1 $\pi_u$ , 3 $\sigma_g$ , and 1 $\pi_g$  with eight electrons. The MCSCF energy is -109.0804 a.u. The wave function  $\Psi^{IV}$  has an active space of 3-4 $\sigma_g$ , 2-3 $\sigma_u$ , 1-3 $\pi_u$ , and 1-2 $\pi_g$ . The MCSCF energy is -109.1740 a.u. Wave functions  $\Psi^I$  and  $\Psi^{II}$  have 396 terms using D<sub>∞h</sub> symmetry,  $\Psi^{III}$  has 21 terms using D<sub>2h</sub> symmetry, and  $\Psi^{IV}$  has 34,721 terms using D<sub>2h</sub> symmetry. Comparisons are made in Table V with the multiconfigurational electron propagator MCEP, GF calculations, and experimental values. The calculations with basis sets I and II show the difference in EKT ionization energies that are obtained using two different basis sets with the same level of calculation. Basis set II includes more diffuse orbitals and gives a better EKT ionization potential than the corresponding calculation using basis set I. The EKT results from  $\Psi^{III}$  are similar to those of Nichols et al.<sup>11</sup> in a similar basis. Significant improvements in the 3 $\sigma_g$  and 1 $\pi_u$  EKT IPs are made by including the additional active orbitals used in  $\Psi^{IV}$ , but the 2 $\sigma_u$  IP is worse. The EKT ionization energies for the 3 $\sigma_g$  and 1 $\pi_u$  from  $\Psi^{IV}$  are comparable to the MCEP values.

## CO

Four MCSCF wave functions were calculated for CO at the equilibrium internuclear distance of  $R_{\text{CO}} = 1.128$  Å. The first,  $\Psi^I$ , was calculated in the DZP basis using an active space of 1-6 $\sigma$  and 1-2 $\pi$  orbitals and an excitation level of 6. The second,  $\Psi^{II}$ , was calculated in the DZP basis with an excitation level of 2 using an active space of 1-8 $\sigma$  and 1-3 $\pi$ , and frozen virtual orbitals 9-10 $\sigma$  and 4 $\pi$ . The third,  $\Psi^{III}$ , was a CAS calculation in the DZP basis with core orbitals 1-4 $\sigma$  and an active space of 5-8 $\sigma$  and 1-3 $\pi$  orbitals. The fourth,  $\Psi^{IV}$ , is a CAS MCSCF wave function in the TZP basis with 1-3 $\sigma$  core or-

**Table V.** Ionization potentials for N<sub>2</sub> in eV.

	EKT( $\Psi^I$ )	EKT( $\Psi^{II}$ )	EKT( $\Psi^{III}$ )	EKT( $\Psi^{IV}$ )	KT	GF <sup>a</sup>	MCEP <sup>b</sup>	Exp. <sup>c</sup>
3 $\sigma_g$	16.37	16.13	16.84	15.66	17.24	15.31	15.52	15.60
1 $\pi_u$	17.01	16.91	17.59	17.22	16.73	16.80	17.24	16.98
2 $\sigma_u$	20.12	20.05	20.98	21.26	21.13	19.01	18.56	18.78

<sup>a</sup>Ref. 28.<sup>b</sup>Ref. 11.<sup>c</sup>Ref. 21.**Table VI.** Ionization potentials for CO in eV.

	EKT( $\Psi^I$ )	EKT( $\Psi^{II}$ )	EKT( $\Psi^{III}$ )	EKT( $\Psi^{IV}$ )	KT	GF <sup>a</sup>	Exp. <sup>b</sup>
5 $\sigma$	14.60	14.32	14.32	14.10	15.00	13.82	14.01
1 $\pi$	17.61	17.43	17.32	17.36	17.38	17.10	16.85
4 $\sigma$	22.11	20.80	21.88	22.14	21.82	19.64	19.78

<sup>a</sup>Ref. 20.<sup>b</sup>Ref. 21.

bitals and an active space of 4-7 $\sigma$  and 1-5 $\pi$  orbitals. There are 1378 configurations in  $\Psi^I$ , 402 configurations in  $\Psi^{II}$ , 1308 in  $\Psi^{III}$ , and 69,001 in  $\Psi^{IV}$  using C<sub>2v</sub> symmetry. The SCF energy in the DZP basis is -112.7590 a.u. and in the TZP basis is -112.7755 a.u. The MCSCF energies are  $E(\Psi^I) = -112.8894$  a.u.,  $E(\Psi^{II}) = -112.9378$  a.u.,  $E(\Psi^{III}) = -112.8331$  a.u., and  $E(\Psi^{IV}) = -112.9643$  a.u. The results given in Table VI show that the lowest EKT ionization potentials have about the same degree of accuracy as the Green's function calculation. The other EKT values are not much different from the KT values.

## HNC

Two MCSCF wave functions were calculated for HNC at the equilibrium internuclear distances  $R_{\text{HN}} = 0.994$  Å and  $R_{\text{NC}} = 1.169$  Å, using the DZP basis set. The wave function  $\Psi^I$  was calculated using an active space 1-8 $\sigma$ , and 1-3 $\pi$  orbitals and a frozen virtual space of 8-9 $\sigma$  and 4 $\pi$  orbitals with an excitation level of 2. The wave function  $\Psi^{II}$  is a CAS MCSCF wave function with core orbitals 1-4 $\sigma$  and with six electrons in an active space of 5-8 $\sigma$  and 1-3 $\pi$  orbitals. The wave function  $\Psi^I$  contains 402 configurations and  $\Psi^{II}$  contains 1308 configurations counted using C<sub>2v</sub> symmetry. The SCF energy in the DZP basis is -92.8744 a.u. and the MCSCF energies are  $E(\Psi^I) = -93.0413$  a.u. and  $E(\Psi^{II}) = -93.0061$  a.u. The lowest EKT IPs are compared with the KT, GF, and experimental IPs in Table VII. Both EKT values are more accurate than the GF value and the EKT IP obtained with the CAS wave function is a considerable improvement over the EKT value obtained using the wave function having an excitation level of 2. Both EKT values are considerable improvements over the KT IPs.

## HCN

Two MCSCF wave functions were calculated for HCN at the equilibrium internuclear distances  $R_{\text{CH}} = 1.065$  Å and  $R_{\text{CN}} = 1.153$  Å, in the DZP basis set. The first,  $\Psi^I$ , was obtained using an active set of 1-9 $\sigma$  and 1-3 $\pi$  orbitals, and a 4 $\pi$  frozen virtual orbital with an excitation level of 2. The second,  $\Psi^{II}$ , is a CAS MCSCF wave function with core orbitals 1-3 $\sigma$ , an active space of 4-8 $\sigma$  and 1-3 $\pi$  orbitals and the 9 $\sigma$  as a frozen virtual orbital. The SCF energy in the DZP basis set is -92.8893 a.u. and the MCSCF energies are  $E(\Psi^I) = -93.0788$  a.u. and  $E(\Psi^{II}) = -93.0609$  a.u. There are 545 configurations in  $\Psi^I$  and 8412 configurations in  $\Psi^{II}$ . The EKT IPs are compared with KT, GF, and experimental values in Table VIII. The numerical value of the lowest EKT IPs are worse than the KT or GF values. Here the lowest KT ionization potential is unusually close to the experimental value, indicating a near cancellation of the correlation and relaxation errors.

**Table VII.** Ionization potentials for HNC in eV.

	EKT( $\Psi^I$ )	EKT( $\Psi^{II}$ )	KT	GF <sup>a</sup>	Exp. <sup>b</sup>
1 $\pi$	13.04	12.76	13.25	11.77	12.55

<sup>a</sup>Ref. 29.<sup>b</sup>Ref. 30.**Table VIII.** Ionization potentials for HCN in eV.

	EKT( $\Psi^I$ )	EKT( $\Psi^{II}$ )	KT	GF	Exp. <sup>a</sup>
1 $\pi$	13.97	14.03	13.51	13.50	13.607
5 $\sigma$	14.77	15.66	15.85	13.92	14.011
4 $\sigma$	21.99	21.90	22.13	20.49	20.1 <sup>b</sup>
3 $\sigma$	32.93	32.96	33.77	31.0	—

<sup>a</sup>Ref. 31.<sup>b</sup>Ref. 21.

**Table IX.** Ionization potentials for C<sub>2</sub>H<sub>2</sub> in eV.

	EKT( $\Psi^I$ )	EKT( $\Psi^{II}$ )	EKT( $\Psi^{III}$ )	EKT( $\Psi^{IV}$ )	KT	GF <sup>a</sup>	Exp. <sup>a</sup>
1 $\pi_u$	11.42	11.22	11.32	11.48	11.15	11.17	11.49
3 $\sigma_g$	18.48	17.81	18.09	18.11	18.47	17.07	16.7
2 $\sigma_u$	20.85	20.26	20.87	20.83	20.90	19.10	18.7
2 $\sigma_g$	28.18	27.50	27.58	27.51	28.03	23.83	23.5
						28.82	27.6 <sup>b</sup>

<sup>a</sup>Ref. 26.<sup>b</sup>Ref. 32.**Table X.** Ionization potentials for H<sub>2</sub>CO in eV.

	EKT( $\Psi^I$ )	EKT( $\Psi^{II}$ )	KT	GF <sup>a</sup>	Exp. <sup>b</sup>
2b <sub>2</sub>	11.33	11.00	11.98	10.84	10.9
1b <sub>1</sub>	15.24	15.00	14.56	14.29	14.5
5a <sub>1</sub>	18.03	17.51	17.68	16.39	16.1
1b <sub>2</sub>	18.31	18.20	18.80	17.25	17.0
4a <sub>1</sub>	23.51	23.32	23.56	21.39	21.4
3a <sub>1</sub>	38.46	38.24	38.26	36.30	34.2

<sup>a</sup>Ref. 20.<sup>b</sup>Ref. 33.

## C<sub>2</sub>H<sub>2</sub>

Four MCSCF wave functions were calculated for C<sub>2</sub>H<sub>2</sub> at the equilibrium internuclear distances  $R_{CC} = 1.203$  Å and  $R_{CH} = 1.061$  Å. The first,  $\Psi^I$ , is from an active space of 1-4 $\sigma_g$ , 1-4 $\sigma_u$ , 1-2 $\pi_u$ , and 1 $\pi_g$  in the DZP basis with an excitation level of 2. The second,  $\Psi^{II}$ , is from an active space of 1-7 $\sigma_g$ , 1-6 $\sigma_u$ , 1-3 $\pi_u$ , and 1-2 $\pi_g$  in the DZP basis with an excitation level of 2. The third,  $\Psi^{III}$ , is a CAS wave function with an inactive space of 1-2 $\sigma_g$  and 1 $\sigma_u$ , and an active space of 3-4 $\sigma_g$ , 2-4 $\sigma_u$ , 1-3 $\pi_u$ , and 1-2 $\pi_g$  in the DZP basis. The fourth,  $\Psi^{IV}$ , is a CAS wave function in the TZP basis using the same core and active space as  $\Psi^{III}$ . The SCF energy in the DZP basis set is -76.8322 a.u. and in the TZP basis is -76.8467 a.u. The MCSCF energies are  $E(\Psi^I) = -76.9878$  a.u.,  $E(\Psi^{II}) = -77.0432$  a.u.,  $E(\Psi^{III}) = -76.9813$  a.u., and  $E(\Psi^{IV}) = -77.0013$  a.u. There 214 configurations in  $\Psi^I$ , 1065 in  $\Psi^{II}$ , and 34,721 in  $\Psi^{III}$  and  $\Psi^{IV}$  using D<sub>2h</sub> symmetry. The results are compared with KT, GF, and experimental values in Table IX. The EKT ionization potential for 1 $\pi_u$  for all four wave functions are significant improvements over the KT value, but the other EKT IPs are not much different from the KT values. The CAS wave func-

tion in the TZP basis is especially close to the experimental value.

## H<sub>2</sub>CO

Two MCSCF wave functions were calculated for H<sub>2</sub>CO at the equilibrium geometry of  $R_{CH} = 1.116$  Å,  $R_{CO} = 1.208$  Å, and  $\theta_{HCH} = 116.5^\circ$  in the DZP basis set. The first wave function,  $\Psi^I$ , is from an active space of 1-9a<sub>1</sub>, 1-3b<sub>1</sub>, and 1-4b<sub>2</sub> with an excitation level of 2. The second,  $\Psi^{II}$ , is a CAS MCSCF wave function with six electrons in an active space of 5-8a<sub>1</sub>, 1-3b<sub>1</sub>, and 2-4b<sub>2</sub>. The number of configurations in  $\Psi^I$  is 279 and in  $\Psi^{II}$  is 1308. The MCSCF energies are  $E(\Psi^I) = -114.0390$  a.u. and  $E(\Psi^{II}) = -114.0338$  a.u. The SCF energy in this basis is -113.8903 a.u. Calculated ionization potentials are compared with experimental values in Table X. The lowest EKT ionization potentials are significant improvements over the KT value.

## B<sub>2</sub>H<sub>6</sub>

An MCSCF wave function was calculated for B<sub>2</sub>H<sub>6</sub> at the equilibrium geometry  $R_{BB} = 1.763$  Å,  $R_{BH} = 1.201$  Å,  $R_{BH'} = 1.32$  Å,  $\theta_{HBH} = 121.0^\circ$ , and  $\theta_{H'BH'} = 96.2^\circ$ , where H' and H refer to the bridging and terminal hydrogens, respectively. The DZP basis set was used with frozen core orbitals 1-2a<sub>g</sub> and 1-2b<sub>1u</sub>, active orbitals 3-4a<sub>g</sub>, 1b<sub>2g</sub>, 1-2b<sub>3g</sub>, 3b<sub>1u</sub>, 2b<sub>2u</sub>, and 1-2b<sub>3u</sub> using an excitation level of 8. The wave function contains 1844 configurations. The SCF energy in the DZP basis is -52.8154 a.u. and the MCSCF energy is -52.8806 a.u. The EKT IPs are compared in Table XI with KT, GF, and experimental values. The EKT lowest IP is only a slight improvement over the KT value.

**Table XI.** Ionization potentials for B<sub>2</sub>H<sub>6</sub> in eV.

	EKT	KT	GF <sup>a</sup>	Exp. <sup>a</sup>
1b <sub>3g</sub>	12.59	12.67	11.92	11.9
3a <sub>g</sub>	14.12	14.01	13.13	13.5
1b <sub>2u</sub>	14.59	14.56	13.77	13.9
1b <sub>3u</sub>	15.21	15.13	14.44	14.8
2b <sub>1u</sub>	17.18	17.28	16.16	16.1
2a <sub>g</sub>	24.36	24.12	21.80	21.3

<sup>a</sup>Ref. 34.

## CONCLUSIONS

The extended Koopmans' theorem provides a way of calculating ionization energies directly from an MCSCF wave function for the un-ionized molecule, without performing separate calculations on the ion. The calculation requires the diagonalization of the orbital Lagrange multiplier matrix in the metric

of the first-order reduced density matrix. Both matrices are the same size as the basis set and the diagonalization is practically trivial. The algorithm for performing the EKT calculations is easy to implement in current MCSCF computer codes that calculate both the orbital Lagrange multiplier matrix and the first-order reduced density matrix. The time required to calculate the EKT IPs is insignificant compared to the time required to calculate a wave function. The EKT calculation requires only a fraction of a second of CPU time compared to minutes or hours to calculate the wave function.

It appears that accurate values can be obtained for the lowest IPs using the EKT, if the active space is large enough and contains a sufficient number of orbitals with the same symmetry as the orbital corresponding to the lowest IP. The calculations reported here seem to indicate that the orbital basis set is important, and that the type of wave function, whether it is CAS MCSCF or has an excitation level of 2 or 4, is less important as long as a good basis set is used. The best results were obtained with CAS MCSCF wave functions using the largest basis sets and containing 34,721–69,001 terms. They give EKT results for the lowest IPs that differ from the experimental IPs by 0.06 eV for N<sub>2</sub>, 0.09 eV for CO, and 0.01 eV for C<sub>2</sub>H<sub>2</sub>. The results suggest that the DZP basis orbitals may not be adequate for accurate IP calculations using the EKT. Generally the lowest IPs obtained from the EKT are a significant improvement over the KT values, except when the KT values are exceptionally good due to near cancellation of errors, and are comparable to the GF values and to the MCEP value for the N<sub>2</sub>. The EKT IPs corresponding to ionization into excited states of the ion show some improvements over the KT IPs for most cases.

The authors acknowledge many valuable discussions with Professor Robert G. Parr. This work was supported in part by a grant from the National Science Foundation to the University of North Carolina at Chapel Hill.

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