

Extended Koopmans' Theorem Ionization Potentials for Beryllium Atom Shake-Up Transitions

ROBERT C. MORRISON

Department of Chemistry, East Carolina University, Greenville, North Carolina 27858-4353

Abstract

The ionization potentials were calculated for Be using the extended Koopmans' theorem (EKT) using several full configuration interaction (CI) and multiconfigurational-self-consistent-field (MCSCF) wave functions as reference wave functions. The wave functions used account for 89.7–96.7% of the correlation energy. Comparisons are made with experimental values and with ΔCI values calculated as the difference in energy obtained from CI wave functions for Be and Be^+ . The best EKT IP differed from the ΔCI value by 0.0003 eV for the lowest IP and by 0.0006 eV for ionization into the lowest ^2P state of Be^+ . A calculation of ionization into the second ^2P state of Be^+ requires diffuse orbitals that are unimportant in the wave function for the ground state of Be. This results in small natural orbital occupation numbers for natural orbitals needed in the EKT calculation. © 1994 John Wiley & Sons, Inc.

I. Introduction

The Koopmans' theorem [1] provides us with an orbital model for ionization using self-consistent-field (SCF) wave functions. The extended Koopmans' theorem (EKT) [2–4] provides an orbital model for ionization using the exact wave function or accurate correlated wave functions. It is particularly well suited for obtaining ionization potentials (IPs) from multiconfigurational-self-consistent-field (MCSCF) wave functions because the information needed to calculate the EKT ionization energies is also used to determine MCSCF wave functions [5]. The time required to calculate the EKT IPs is insignificant compared to the time required to calculate the MCSCF wave function. Most MCSCF computer programs are easily adapted to perform EKT calculations. Because the MCSCF method is commonly used in quantum chemistry calculations, the EKT is a practical method for obtaining approximate ionization potentials. We have already implemented the EKT method with the ALCHEMY II [6], GAMESS [7], HONDO [8], and SIRIUS [9] computer programs.

The extended Koopmans' theorem gives lowest ionization potentials that are improvements over the Koopmans' theorem IPs, except where the Koopmans' theorem IPs are close to the experimental values because of the near cancellation of errors [10]. It has been demonstrated numerically that the EKT can be used to calculate the lowest IP to arbitrary accuracy when increasingly accurate wave functions are used [11, 12]. Recently, the question of the exactness of the lowest EKT IP [13, 14] has been resolved [15].

In early work [16], there was evidence that the EKT could be used to calculate IPs into some of the low-level excited states of the ions. Shake-up transitions [17] into these states can be viewed in the independent-particle model as the removal of an electron from an occupied valence orbital with the simultaneous excitation of a second valence electron. In this article, we investigate the extent to which the EKT can be used to calculate IPs into the excited states of the ion using accurate MCSCF and configuration interaction (CI) wave functions for the Be atom.

Ionization in the EKT model is viewed as elimination of a variationally determined orbital from a reference wave function of the N -electron system. This can be expressed as

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

or

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

In Eq. (2), \hat{q} is a linear combination of orbital annihilation operators:

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

The annihilation operator \hat{a}_i annihilates orbital ϕ_i from the N -electron wave function. The q 's are found by solving the matrix equations

$$(\mathbf{V} - \varepsilon \boldsymbol{\gamma})\mathbf{c} = \mathbf{0}, \quad (4)$$

where

$$V_{ij} = -\langle \psi^N | \hat{a}_i^\dagger [\hat{H}, \hat{a}_j] | \psi^N \rangle, \quad (5)$$

and the elements of the first-order reduced density matrix are

$$\gamma_{ij} = \langle \psi^N | \hat{a}_i^\dagger \hat{a}_j | \psi^N \rangle. \quad (6)$$

The IPs are the negative of the ε 's obtained from solving Eq. (4).

The matrix $\boldsymbol{\gamma}$ may become ill-conditioned when the natural orbital (NO) occupation numbers become very small. These NOs can be eliminated from the calculation by using canonical orthonormalization in the solution of Eq. (4). However, orbitals that are important for diffuse excited states of the ion may not contribute significantly to the energy of the ground state of the un-ionized system. Therefore, the NOs that are weakly occupied in the ground state of the un-ionized system may be the very ones that are needed for the excited states of the ionized system.

Aside from the fact that the theoretical limit of the accuracy of the EKT method for ionization into excited states is not yet known, there are two limitations in practical calculations. One limitation is the size of the basis set. Most basis sets used in modest calculations for atoms do not contain more than 10 or so s orbitals. The number of p , d , and f orbitals is usually less. Such basis sets may not be adequate when using the EKT to calculate more than 1 or 2 IPs for each symmetry type. The second limitation is the size of the NO occupation numbers. Many excited states of ionized systems require orbitals that do not contribute significantly to the energy of the reference state of

the un-ionized system. Such orbitals would usually be associated with NO occupation numbers that are very small in the ground state of the un-ionized system and would produce ill-conditioned γ 's in the matrix Eq. (4).

II. Calculations and Results

Extended Koopmans' theorem ionization energies were calculated from several wave functions for Be. The first wave function, Ψ_I , is an MCSCF wave function that contains single and double excitations in an orbital basis set of 8 *s*, 7 *p*, 4 *d*, and 3 *f* (8*s*7*p*4*d*3*f*) formed from the set of (10*s*9*p*8*d*7*f*) Slater-type orbitals (STOs) used by Bunge [18] in an accurate CI wave function for the Be atom. All calculations of CI and MCSCF wave functions using STOs were performed using the ALCHEMY II programs [6]. The second wave function, Ψ_{II} , is a complete active space (CAS) MCSCF wave function with a set of (5*s*4*p*2*d*2*f*) active orbitals formed from the STO set of (10*s*9*p*8*d*7*f*) used by Bunge. This wave function accounts for 96.7% of the correlation energy based on a Hartree-Fock energy of -14.5730 au and a best nonrelativistic value not including mass polarization of -14.6673 au [19]. The third wave function, Ψ_{III} , is a CAS MCSCF wave function with 8 *s* and 7 *p* active orbitals using the STO set of (10*s*9*p*). The fourth wave function, Ψ_{IV} , is a full CI wave function using the 8 *s* and first 4 *p* MCSCF orbitals of Ψ_{III} augmented with the 4 *p* STOs in Table I. The set of *p* orbitals has been selected by trial and error to give a good IP into the second 2P state of Be⁺. It has not been systematically optimized to give either the lowest energy or the best ionization energy into the second 2P state of Be⁺. Full optimization of this basis set was too expensive. Wave functions Ψ_{III} and Ψ_{IV} account for 93.5 and 93.0% of the correlation energy, respectively. The fifth wave function, Ψ_V , is a full CI wave function using the contracted Cartesian Gaussian basis set of (7*s*7*p*3*d*) used by Golab and Yeager [20] in their calculation of Be IPs using the multiconfigurational spin tensor electron propagator (MCSTEP) method. The basis set used here differs slightly by including the $x^2 + y^2 + z^2$ combination of *d* functions. The sixth wave function, Ψ_{VI} , is a full CI wave function using the Gaussian basis set (7*s*7*p*) augmented with two additional primitive *s* and *p* orbitals to form a basis set of (9*s*9*p*). The orbital exponents for the additional *s* orbitals are 0.8 and 0.5, and for the additional *p* orbitals, 4.0 and 0.95. Wave functions Ψ_V and Ψ_{VI} account for 89.7% of the correlation energy.

The EKT results are compared with the Δ CI results and experimental values in Table II. Experimental values were obtained from Bashkin and Stoner [21]. The Δ CI results were calculated by taking the difference between the CI energies obtained for the ground state of Be and the CI energies of the Be⁺ states in the same basis. The ionic

TABLE I. The *p* Slater-type orbitals used to augment the MCSCF basis set for wave function Ψ_{IV} .

Orbital	Exponent
2 <i>p</i>	0.50
3 <i>p</i>	0.25
4 <i>p</i>	0.10
3 <i>p</i>	0.05

TABLE II. Be ionization energies from the extended Koopmans' theorem for several wave functions; all values are reported in eV (1 Hartree = 27.212 eV).

Orbital	E_{total} (au)												Exp. ^a						
	$\Psi_I(8s7p4d3f)$			$\Psi_{II}(5s4p2d2f)$			$\Psi_{III}(8s7p)$			$\Psi_{IV}(8s8p)$				$\Psi_V(7s7p3d)$			$\Psi_{VI}(9s9p)$		
	EKT	Δ CI		EKT	Δ CI		EKT	Δ CI		EKT	Δ CI			EKT	Δ CI		EKT	Δ CI	
	-14.6620			-14.6642			-14.6612			-14.6607			-14.6576			-14.6576			
$2S(2s)$	9.24	9.23		9.33	9.33		9.29	9.29		9.2890	9.2887		9.30	9.30		9.29	9.29		9.32
$2S(3s)$	22.23	22.07		23.54	22.98		21.10	21.04		21.10	21.04		20.43	20.23		20.41	20.22		20.26
$2P(2p)$	14.63	13.15		13.53	13.30		13.48	13.31		13.3137	13.3131		13.30	13.26		13.31	13.31		13.28
$2P(3p)$	68.23	28.29		185	43.10		83.91	27.81		21.55	21.26		27.90	21.25		24.15	21.26		21.28
$2D(3d)$	29.33	28.40		37.19	29.24		—	—		—	—		—	—		—	—		21.48
$2F(4f)$	45.92	27.26		44.49	43.57		—	—		—	—		—	—		—	—		24.13

^a[21].

wave functions used for obtaining Δ CI results with Ψ_I consisted of single and double excitations from the dominant reference configuration. The other wave functions for Be^+ are full CI wave functions.

Previous calculations [10] have indicated that complete active space wave functions give slightly better EKT IPs than do wave functions that have only single and double excitations. This can be observed in Table II for the two 2S states and the first 2P state of Be^+ .

The closeness of the EKT to the Δ CI values for the lowest IP is relatively insensitive to the basis set used or the type of wave function. This is expected except for minimal basis sets; all the basis sets used here were more than minimal basis sets. The lowest IP is also insensitive to elimination of NOS with the smallest occupation numbers.

In the following discussion, we use the terms $^2S(3s)$ IP, $^2S(2p)$ IP, etc., to mean ionization potentials for ionization from the ground state of Be to the Be^+ states with dominant configurations $1s^23s$ and $1s^22p$, respectively. The $^2D(3d)$ and $^2F(4f)$ IPs in Table II are not close to experimental values either for the EKT calculations or the Δ CI calculations. This illustrates the need for appropriate basis sets for ionization into excited states of the ion.

A. $^2S(3s)$ IP

The EKT values for ionization to the $^2S(3s)$ state, listed in Table II, differ from the Δ CI values by as much as 0.56 eV for Ψ_{II} and as little as 0.06 eV for Ψ_{III} and Ψ_{IV} . The higher error for Ψ_{II} is attributed to the smaller number of s orbitals used in the calculation. There are only five s -type MCSCF orbitals in Ψ_{II} , whereas there are eight in Ψ_{III} and Ψ_{IV} , suggesting that the better performance of the EKT method for Ψ_{III} and Ψ_{IV} is due to an improved basis set. For those basis sets that contain 8s orbitals, the closeness of the EKT value to the Δ CI value for the $^2S(3s)$ IP is relatively insensitive to the basis set or to omitting the NOS with the smallest occupation numbers. The EKT orbital energies are not near the IPs into higher 2S states of Be^+ and are not reported.

B. $^2P(2p)$ IP

The EKT ionization potentials for ionizations into the first 2P state of Be^+ differ from the corresponding Δ CI values by as little as 0.0006 eV for Ψ_{IV} and as much as 1.48 eV for Ψ_I . The large difference for Ψ_I may be due to including only single and double excitations in the CI expansion. For the full CI and CAS MCSCF wave functions, the closeness of the EKT values to the Δ CI values for the $^2P(2p)$ IP is relatively insensitive to the basis set and to omitting the NOS with the lowest occupation numbers. The accuracy of the lowest 2P ionization is near the accuracy of the lowest IP for the full CI and CAS MCSCF wave functions.

C. $^2P(3p)$ IP

Golab and Yeager [20] observed that a description of the $^2P(3p)$ ionization requires diffuse orbitals in the basis set. None of the EKT orbital energies can be interpreted as the $^2P(3p)$ IP using wave functions Ψ_I , Ψ_{II} , and Ψ_{III} because their basis sets do

not contain the appropriate diffuse orbitals. Therefore, there are large errors in the calculated EKT IPs. There are also large errors in the ΔCI values. Diffuse p functions are included in the basis sets for Ψ_{IV} , Ψ_{V} , and Ψ_{VI} and the corresponding ΔCI values for the $^2P(3p)$ IP are close to the experimental value. The selected addition of diffuse STOs to the basis set for Ψ_{IV} results in a reasonably close value for the EKT IP. However, the smallest NO occupation number is 0.3×10^{-14} , making the metric γ ill-conditioned. The lowest NO occupation numbers are listed in Table III. The results of selectively excluding the NOS with the smallest occupation numbers are given in Table IV. When the two NOS with the smallest occupation numbers are excluded from the calculation using Ψ_{IV} , the predicted EKT IP for this state is in error by nearly 30 eV. These diffuse orbitals, although unimportant in the ground state of Be, are necessary for the ionization into the $^2P(3p)$ excited state of Be^+ . To check for inaccuracies due to inclusion of the NOS with small occupation numbers, the results of calculations that include the NOS with the smallest occupation numbers were checked for stability with respect to changing the convergence criteria of the CI wave function. All digits reported were stable except where noted in Table IV.

III. Discussion

Several MCSCF and full CI wave functions for the ground state of Be were used as reference wave functions for determining EKT ionization potentials. The EKT IPs into the lowest 2S and 2P states of Be^+ are quite accurate and appear to be relatively insensitive with respect to choice of basis set as long as it is extensive enough to obtain good energies for the ground state of Be. The $^2S(3s)$ IP is also relatively insensitive to the choice of basis set, but it is not calculated quite as accurately as the $^2S(2s)$ and $^2P(2p)$ IPs. Whether the accuracy is limited by the size of the basis sets or whether there is a theoretical limitation is not known. The calculation of the $^2P(3p)$ IP depends more strongly on the choice of basis set because a description of this ionization requires diffuse orbitals that are unimportant in the ground-state calculation of Be. This can be problematic for the EKT because unimportant orbitals lead to small occupation numbers. These small occupation numbers result in an ill-conditioned metric γ in Eq. (4). In spite of these numerical problems, the EKT value of the $^2P(3p)$ IP differs by only 0.3 eV from the ΔCI and experimental values.

TABLE III. The smallest natural orbital occupation numbers for wave functions Ψ_{IV} and Ψ_{VI} .

Ψ_{IV}		Ψ_{VI}	
Orbital	n_i	Orbital	n_i
p	0.34×10^{-14}	p	0.93×10^{-13}
p	0.33×10^{-11}	s	0.75×10^{-11}
p	0.91×10^{-9}	p	0.64×10^{-8}
p	0.39×10^{-5}	s	0.19×10^{-7}

TABLE IV. A comparison of Be ionization energies from the extended Koopman's theorem with selective elimination of the natural orbitals with the smallest occupation numbers.

	Ψ_{IV}			Ψ_{VI}	
	Nos omitted				
	(2 <i>p</i>)	(1 <i>p</i>)	None	(1 <i>s</i> , 2 <i>p</i>)	None
$^2S(2s)$	9.29	9.29	9.29	9.29	9.29
$^2S(3s)$	21.10	21.10	21.10	20.41	20.41
$^2P(2p)$	13.35	13.31	13.31	13.31	13.31
$^2P(3p)$	50.42	21.60	21.55	24.15	23.6(9) ^a

^aThe digit in parentheses was not stable with respect to changing the convergence criteria for the CI wave function.

In modest-sized basis sets, the number of orbital variational parameters in an EKT calculation is very small compared to the number of configurations in the wave function for the ionized system. For example, the *s* block of **V** in Eq. (4) is a 7×7 block for the (7*s*7*p*3*d*) basis set of Ψ_V , whereas there are 5080 configurations using D_{2h} symmetry in the wave function for the 2S state of Be⁺ in this basis set. One should therefore not expect to obtain more than a few of the lowest IPs using the EKT. The orbital operator, *q*, has only annihilation operators. To obtain higher IPs within this framework, higher-order operators involving products of creation and annihilation operators are needed. For example, to accurately calculate IPs from MCSCF wave functions, Golab and Yeager [20] used the annihilation operators plus triple operators consisting of products of a creation operator and two annihilation operators in the MCSTEP method.

The proof for the exactness of the EKT for the lowest IP is based on the asymptotic behavior of the density [13]. Based on this proof, one expects to be able to obtain the lowest IP to arbitrary accuracy. The difference between the EKT value of the $^2P(3p)$ IP and the Δ CI value for wave function Ψ_{IV} is 0.0006 eV, suggesting that the $^2P(2p)$ ionization can also be obtained to arbitrary accuracy. For Be, the asymptotic behavior of each Hartree–Fock *s* orbital is governed by the orbital energy [22, 23]. One might question to what extent this influences the accuracy of the EKT IPs for Be.

Acknowledgments

I have had the opportunity to spend some time in Professor Parr's laboratory several times over the last few years. During my first visit to Chapel Hill for a one-semester sabbatical, I was uncertain about my return to quantum chemistry after doing research in other areas for about 10 years. That uncertainty quickly disappeared under Professor Parr's inspiration and guidance. He rekindled my interest in the extended Koopmans' theorem, and our many discussions and collaboration led to the resolution of the question surrounding its exactness. The author is grateful to M. Yoshimine and A. D. McLean for the IBM RS6000 version of the ACHELMY II programs.

Bibliography

- [1] T. A. Koopmans, *Physica* **1**, 104 (1933).
- [2] O. W. Day, D. W. Smith, and C. Garrod, *Int. J. Quantum Chem. Symp.* **8**, 501 (1974).
- [3] D. W. Smith and O. W. Day, *J. Chem. Phys.* **62**, 113 (1975).
- [4] M. M. Morrell, R. G. Parr, and M. Levy, *J. Chem. Phys.* **62**, 549 (1975).
- [5] J. Hinze, *J. Chem. Phys.* **59**, 6424 (1973).
- [6] A. D. McLean, M. Yoshimine, B. H. Lengsfeld, P. S. Bagus, and B. Liu, in *Modern Techniques in Computational Chemistry*, E. Clementi, Ed. (Escom, Leiden, 1990), p. 593.
- [7] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, J. H. Jensen, S. Koseki, M. S. Gordon, K. A. Nguyen, T. L. Windus, and S. T. Elbert, *QCPE Bull.* **10**, 52 (1990).
- [8] M. Dupuis, A. Farazdel, S. P. Karna, and S. A. Maluendes, in *Modern Techniques in Computational Chemistry*, E. Clementi, Ed. (Escon, Leiden, 1990), p. 227.
- [9] H. A. Jensen, H. Ågren, and J. Olsen, in *Modern Techniques in Computational Chemistry*, E. Clementi, Ed. (Escom, Leiden, 1990), p. 435.
- [10] R. C. Morrison and G. Liu, *J. Comput. Chem.* **13**, 1004 (1992).
- [11] R. C. Morrison, *J. Chem. Phys.* **96**, 3718 (1992).
- [12] D. Sundholm and J. Olsen, *J. Chem. Phys.* **98**, 3999 (1993).
- [13] J. Katriel and E. R. Davidson, *Proc. Natl. Acad. Sci. U.S.A.* **77**, 4403 (1980).
- [14] B. T. Pickup and J. G. Snijders, *Chem. Phys. Lett.* **153**, 69 (1988).
- [15] R. C. Morrison, Z. Zhou, and R. G. Parr, *Theor. Chem. Acta* **86**, 3 (1993).
- [16] O. W. Day, D. W. Smith, and R. C. Morrison, *J. Chem. Phys.* **62**, 115 (1975).
- [17] R. L. Martin and D. W. Shirley, in *Electron Spectroscopy, Theory, Techniques, and Applications*, C. R. Brundle and A. D. Baker, Eds. (Academic Press, New York, 1977), p. 76.
- [18] C. F. Bunge, *At. Data Nucl. Data Tables* **18**, 293 (1976).
- [19] C. F. Bunge, *Phys. Rev. A* **14**, 1965 (1976).
- [20] J. T. Golab and D. L. Yeager, *J. Chem. Phys.* **87**, 2925 (1987).
- [21] S. Bashkin and J. A. Stoner, Jr., *Atomic Energy Levels and Grottrian Diagrams* (North-Holland, New York, 1975), Vol. 1.
- [22] N. C. Handy, M. T. Marron, and H. J. Silverstone, *Phys. Rev.* **180**, 45 (1969).
- [23] T. Ishida and K. Ohno, *Theor. Chem. Acta* **81**, 355 (1992).

Received April 6, 1993

Revised manuscript received October 7, 1993

Accepted for publication October 11, 1993