Examination of the Limits of Accuracy of the Extended Koopmans' Theorem Ionization Potentials into Excited States of Ions of LiH, He₂, and Li₂

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Abstract

A comparison is made between the ionization potentials (IPs) calculated by the extended Koopmans' theorem (EKT) and by taking energy differences (ΔCI) from configuration interaction calculations in the same basis. Several ionization potentials were calculated for LiH, He₂, and Li₂. The best ΔIP, the difference between the EKT IP and the corresponding ΔCI value, was 0.05 meV for the 2σ orbital for LiH and 83.5 meV for the 3σ orbital. The ΔIPs for He₂ were 0.7 meV for the $1\sigma_u$ orbital, 6 eV for the $2\sigma_u$ orbital, 5 meV for the $2\sigma_g$ orbital, and 3 eV for the $3\sigma_g$ orbital. The ΔIPs for Li₂ are 0.1 meV for $2\sigma_g$, 53 meV for $3\sigma_g$, 0.6 meV for $2\sigma_u$, and 1.73 eV for $3\sigma_u$. © 1994 John Wiley & Sons, Inc.

Introduction

The extended Koopman's theorem (EKT) [1–3] provides a method of calculating ionization potentials (IPs) from certain classes of reference wave functions which go beyond the independent particle model. Such wave functions include multi-configurational-self-consistent field (MCSCF) wave functions, full configuration interaction wave functions, and complete-active-space-self-consistent field wave functions. The EKT can be considered to be a special case of the electron propagator and Green's function methods [4–8].

There has been considerable interest [9–16] in the question of the exactness of the EKT for the lowest ionization potential. It has been demonstrated numerically that the lowest EKT IP is exact [11,13]. There is also numerical evidence the EKT is exact for IPs besides the lowest one [15,16].

The EKT IPs are found by solving the matrix equations

$$(\mathbf{V} - \varepsilon\gamma)\mathbf{c} = \mathbf{0} , \tag{1}$$

where

$$V_{ij} = -\left\langle \Psi^N \,|\, \hat{a}_i^\dagger [\hat{H}, \hat{a}_j] \,|\, \Psi^N \right\rangle . \tag{2}$$

We can consider $\hat{a}_i$ to annihilate the ith natural spin orbital (NSO) of $|\Psi^N\rangle$ to form an $(N-1)$-electron wave function $|\Phi_i^{N-1}\rangle$:

$$|\Phi_i^{N-1}\rangle = \hat{a}_i|\Psi^N\rangle \, .$$

The $|\Phi_i^{N-1}\rangle$ form the basis for the $(N-1)$-electron wave function, although the $(N-1)$-electron wave function is not calculated explicitly. The matrix γ is the overlap matrix of the $|\Phi_i^{N-1}\rangle$ and in the NSO-derived basis is a diagonal matrix of NSO occupation numbers n_i,

$$n_i = \gamma_{ii} = \langle \Psi^N | \hat{a}_i^\dagger \hat{a}_i | \Psi^N \rangle \, . \tag{3}$$

It is well known that for the ground states of most atoms and molecules N of the n_i are near 1 and the rest fall off very rapidly toward zero. It is not known whether any are actually zero for ground states of many-electron atoms and molecules. It is believed that none of the n_i are zero for ground states of 2-electron systems [12]. Although it has been assumed that some n_i might be zero for ground states of many-electron systems [17], it is unlikely that any are identically zero [12]. Related questions are whether or not the generalized overlap amplitudes, also called Feynman Dyson amplitudes, are linearly independent [18], whether or not the $|\Phi_i^{N-1}\rangle$ form a complete set, and whether or not the set of eigenfunctions having nonzero eigenvalues of the $(N-1)$-particle reduced density matrix form a complete set [17]. Although we do not expect the EKT calculations to answer these questions, whether or not all the EKT IPs are exact depends on their answers.

The fact that the smallest n_i rapidly decreases as the size of the basis set is increased causes Eq. (1) to become ill-conditioned. Thus EKT calculations using large basis sets which result in a number of very small n_i become difficult and seemingly impractical. We have used canonical orthonormalization to eliminate $|\Phi_i^{N-1}\rangle$ corresponding to n_i below a certain threshold. However, this discards information which might be critical for obtaining accurate ionization potentials.

In this article we examine several IPs for He_2, LiH, and Li_2 by carrying out a series of calculations in which basis set sizes are varied. Basis sets are systematically changed from one calculation to the next by including additional SCF virtual orbitals in the set.

Calculations and Results

All calculations were performed using the GAMESS [19] program. The basis sets for He and Li were taken from Rizzo, Clementi, and Sekiya [20]. The basis set for H is the same as that used in a previous calculation on H_5^+ [11]. Self-consistent field calculations were performed on each of the three molecules He_2, LiH, and Li_2. The SCF orbitals were systematically included in full CI calculations on the ground state of the neutral molecules He_2, LiH, and Li_2, and on several states of the positive ions He_2^+, LiH$^+$, and Li_2^+.

The number of orbitals included in the calculations ranged from 3–18 for He_2, 3–23 for LiH, and 4–16 for Li_2. In order to avoid numerical difficulties the $(N-1)$-electron basis functions, $|\Phi_i^{N-1}\rangle$, were excluded from the basis set for most of the calculations if the corresponding NSO occupation was smaller than 10^{-8}. This excludes many of the $(N-1)$-electron basis functions for the larger orbital basis

sets. For comparison several calculations were performed using smaller n_i tolerances for excluding the $|\Phi_i^{N-1}\rangle$.

The ionization energies were calculated using both the EKT method and by taking the energy difference IP(ΔCI) of full CI calculations on the neutral molecule and on the ion in the same basis set.

In the work of Sundholm and Olsen [13] the best comparison between EKT IPs and ΔCI IPs was obtained using only s orbitals. If the higher EKT IPs involving ionization from σ orbitals LiH, He$_2$, and Li$_2$ are exact it should be apparent even when only s orbitals are in the basis set. In order to include as many s orbitals as possible within the constraints of our computer system most of the calculations were performed using only s orbitals. For comparison one calculation which includes p orbitals was performed on LiH.

The results of calculations for LiH, He$_2$, and Li$_2$ are given in Tables I, II, and III, respectively. The first column lists the number of SCF orbitals included in the basis set for the full CI calculation. The number of natural orbitals kept in the EKT calculation is given in parentheses. The IPs are labeled by the EKT orbital. For example 2σ for LiH corresponds to ionization into the $^2\Sigma^+(1\sigma^2 2\sigma)$ state of LiH$^+$, 3σ corresponds to ionization into the $^2\Sigma^+(1\sigma^2 3\sigma)$ state of LiH$^+$, $1\sigma_u$ for He$_2$ corresponds to ionization into the $^2\Sigma_g^+(1\sigma_g^2 1\sigma_u)$ state of He$_2^+$, and $2\sigma_g$ for Li$_2$ corresponds to ionization into the $^2\Sigma_g^+(1\sigma_g^2 1\sigma_u^2 2\sigma_g)$ state of Li$_2$, etc.

TABLE I. A comparison of the EKT and ΔCI ionization potentials for LiH for increasingly larger basis sets. The natural orbital occupation tolerance for excluding natural orbitals is 10^{-8}. The internuclear distance is 1.5955 Å.

Orbitals SCF (NOS)	Energy	2σ			3σ		
		ΔCI	EKT	ΔIP	ΔCI	EKT	ΔIP
5σ (3σ)	-7.97210	7.9783	7.9789	0.0006	21.9230	21.9765	0.0535
10σ (6σ)	-7.97814	7.5534	7.5535	0.00006	19.1115	19.2642	0.1528
12σ (8σ)	-7.98916	7.3641	7.3641	0.00004	19.1409	19.1901	0.0492
15σ (11σ)	-8.00022	7.3748	7.3748	0.00003	19.2091	19.2908	0.0816
19σ (15σ)	-8.00734	7.3808	7.3809	0.00004	19.2138	19.2959	0.0822
23σ (17σ)	-8.00788	7.3811	7.3812	0.00005	19.2138	19.2972	0.0835
$15\sigma 6\pi$ ($8\sigma 2\pi$)	-7.99137	7.6553	7.6554	0.00008	19.8188	20.1706	0.3519

Orbitals SCF (NOS)	Energy	4σ			5σ		
		ΔCI	EKT	ΔIP	ΔCI	EKT	ΔIP
5σ (3σ)	-7.97210	26.6495	67.2539	40.6043	—	—	—
10σ (6σ)	-7.97814	22.2983	23.0676	0.7694	24.7488	27.9142	3.1654
12σ (8σ)	-7.98916	22.0029	22.1765	0.1736	24.5706	30.0822	5.5116
15σ (11σ)	-8.00022	22.0496	22.3935	0.3439	24.6318	30.0280	5.3962
19σ (15σ)	-8.00734	22.0565	22.3864	0.3299	24.6385	30.1374	5.4988
23σ (17σ)	-8.00788	22.0568	22.4621	0.4053	24.6388	30.1537	5.5149
$15\sigma 6\pi$ ($8\sigma 2\pi$)	-7.99137	22.7876	23.5631	0.7755	24.4740	27.0050	2.5310

TABLE II. A comparison of EKT and ΔCI ionization potentials for He_2. The natural orbital threshold for excluding natural orbitals is 10^{-8}, except where noted. The internuclear distance is 1.08 Å.

Orbitals SCF (NO)	Energy	$1\sigma_u$			$2\sigma_u$		
		ΔCI	EKT	ΔIP	ΔCI	EKT	ΔIP
$2\sigma_g2\sigma_u$ $(1\sigma_g1\sigma_u)$	−5.60963	19.8741	19.8750	0.0008	—	—	
$3\sigma_g3\sigma_u$ $(2\sigma_g2\sigma_u)$	−5.60964	19.8692	19.8696	0.0003	53.2231	69.4167	16.1937
$4\sigma_g4\sigma_u$ $(2\sigma_g2\sigma_u)$	−5.60964	19.8518	19.8525	0.0007	51.9285	66.1611	14.2327
$5\sigma_g5\sigma_u$ $(2\sigma_g2\sigma_u)$	−5.60967	19.8026	19.8047	0.0021	50.6575	64.5225	13.8651
$6\sigma_g6\sigma_u$ $(2\sigma_g2\sigma_u)$	−5.60986	19.6890	19.6947	0.0057	49.4427	63.6271	14.1843
$7\sigma_g7\sigma_u$ $(3\sigma_g2\sigma_u)$	−5.61078	19.4876	19.4892	0.0017	48.3200	51.9340	3.6140
$8\sigma_g8\sigma_u$ $(3\sigma_g3\sigma_u)$	−5.61391	19.2335	19.2343	0.0008	44.9955	51.8642	6.8687
$9\sigma_g8\sigma_u$ $(3\sigma_g4\sigma_u)$	−5.61713	19.1230	19.1235	0.0005	44.8019	50.1532	5.3513
$9\sigma_g8\sigma_u$ $(5\sigma_g6\sigma_u)^a$	−5.61713	19.1230	19.1235	0.0005	44.8019	50.1327	5.3308
$9\sigma_g9\sigma_u$ $(4\sigma_g4\sigma_u)$	−5.62075	19.0037	19.0038	0.0001	44.4116	51.5217	7.1101
$9\sigma_g9\sigma_u$ $(7\sigma_g6\sigma_u)^b$	−5.62075	19.0037	19.0044	0.0007	44.4116	50.0672	5.6556

Orbitals SCF (NO)	Energy	$2\sigma_g$			$3\sigma_g$		
		ΔCI	EKT	ΔIP	ΔCI	EKT	ΔIP
$2\sigma_g2\sigma_u$ $(1\sigma_g1\sigma_u)$	−5.60963	30.0663	30.0671	0.0008	—	—	—
$3\sigma_g3\sigma_u$ $(2\sigma_g2\sigma_u)$	−5.60964	30.0612	30.0614	0.0002	51.9024	73.4326	21.5302
$4\sigma_g4\sigma_u$ $(2\sigma_g2\sigma_u)$	−5.60964	30.0420	30.0428	0.0007	50.2310	71.3962	21.1651
$5\sigma_g5\sigma_u$ $(2\sigma_g2\sigma_u)$	−5.60967	29.9858	29.9882	0.0024	48.6722	69.9379	21.2656
$6\sigma_g6\sigma_u$ $(2\sigma_g2\sigma_u)$	−5.60986	29.8520	29.8587	0.0067	47.2402	69.0186	21.7784
$7\sigma_g7\sigma_u$ $(3\sigma_g2\sigma_u)$	−5.61078	29.6050	29.6062	0.0012	45.9840	56.9979	11.0139
$8\sigma_g8\sigma_u$ $(3\sigma_g3\sigma_u)$	−5.61391	29.2706	29.2734	0.0029	47.3676	58.3577	10.9901
$9\sigma_g8\sigma_u$ $(3\sigma_g4\sigma_u)$	−5.61713	29.1061	29.1109	0.0048	47.0126	60.1247	13.1121
$9\sigma_g8\sigma_u$ $(5\sigma_g6\sigma_u)^a$	−5.61713	29.1061	29.1086	0.0025	47.0126	57.1854	10.1728
$9\sigma_g9\sigma_u$ $(4\sigma_g4\sigma_u)$	−5.62075	28.9410	28.9488	0.0077	46.7567	57.5458	10.7891
$9\sigma_g9\sigma_u$ $(7\sigma_g6\sigma_u)^b$	−5.62075	28.9410	28.9461	0.0051	46.7567	50.0604	3.3037

^{a} Natural orbital occupation threshold is 10^{-12}.
^{b} Natural orbital occupation threshold is 10^{-13}.

LiH

For the case using 23 σ SCF orbitals and 17 σ NO's the ΔIP for the lowest IP, 2σ, is 0.05 meV whereas the ΔIP for the next IP, 3σ, is 83.5 meV. The lowest IP is 1670 times more accurate than the next one. The 4σ EKT IP is about five times less accurate than the 3σ EKT IP and the 5σ IP is an order of magnitude less accurate than the 4σ EKT IP. Adding p orbitals to the basis set does not significantly improve the accuracy of the EKT IPs. Lowering the n_i threshold to 10^{-10} for exclusion of $|\Phi_i^{N-1}\rangle$ gives negative ΔIPs in some cases (not shown in the table). This illustrates the problem of including $|\Phi_i^{N-1}\rangle$ with small n_i in the EKT calculation.

He_2

The results for He_2 are given in Table II. The best ΔIP values for the lowest IP, $1\sigma_u$, are 0.1 meV to 0.7 meV whereas the best ΔIP for the $2\sigma_u$ is 5.6 eV, about 8000

TABLE III. A comparison of EKT and ΔCI ionization potentials for Li_2. The natural orbital occupation tolerances for excluding natural orbitals are 10^{-8}. The internuclear distance is 2.6731 Å.

Orbital space SCF (NO)	Total energy	$2\sigma_g$			$3\sigma_g$		
		ΔCI	EKT	ΔIP	ΔCI	EKT	ΔIP
$4\sigma_g4\sigma_u$ $(3\sigma_g2\sigma_u)$	−14.86434	5.1457	5.1463	0.0006	13.3540	15.8394	2.4854
$5\sigma_g5\sigma_u$ $(3\sigma_g3\sigma_u)$	−14.86657	5.1897	5.1901	0.0005	12.5370	13.0719	0.5349
$6\sigma_g6\sigma_u$ $(4\sigma_g3\sigma_u)$	−14.87012	5.2358	5.2366	0.0008	11.7940	12.1503	0.3563
$7\sigma_g7\sigma_u$ $(5\sigma_g4\sigma_u)$	−14.87419	5.2582	5.2584	0.0002	11.2485	11.3375	0.0890
$8\sigma_g8\sigma_u$ $(5\sigma_g5\sigma_u)$	−14.87658	5.2778	5.2779	0.0001	11.1113	11.1643	0.0531

SCF (NO)	Energy	$2\sigma_u$			$3\sigma_u$		
		ΔCI	EKT	ΔIP	ΔCI	EKT	ΔIP
$4\sigma_g4\sigma_u$ $(3\sigma_g2\sigma_u)$	−14.86434	9.3520	9.3716	0.0196	13.9851	67.3533	53.3682
$5\sigma_g5\sigma_u$ $(3\sigma_g3\sigma_u)$	−14.86657	8.8066	8.8352	0.0286	13.3470	67.4025	54.0554
$6\sigma_g6\sigma_u$ $(4\sigma_g3\sigma_u)$	−14.87012	8.3671	8.3807	0.0136	12.7659	28.2091	15.4431
$7\sigma_g7\sigma_u$ $(5\sigma_g4\sigma_u)$	−14.87419	8.1080	8.1082	0.0002	12.3718	13.3395	0.9677
$8\sigma_g8\sigma_u$ $(5\sigma_g5\sigma_u)$	−14.87658	8.0359	8.0365	0.0006	12.2437	13.9737	1.7300

times greater. The ΔIP for the $2\sigma_g$ IP is about 5 meV, about 10 times greater than for the $1\sigma_u$ IP. Both the $1\sigma_u$ and the $2\sigma_g$ IPs can be calculated very accurately.

Li_2

The $2\sigma_g$ ΔIP of 0.1 meV is 530 times less than the 53 meV ΔIP for the $3\sigma_g$ IP. The $2\sigma_g$ IP is about six times more accurate than the $2\sigma_u$ IP. The $3\sigma_u$ EKT IP is considerably worse. As is the case with He_2, the lowest EKT IP of each symmetry type, σ_g and σ_u, can be calculated very accurately, with the lowest IP of the two being an order of magnitude more accurate.

Conclusions

In He_2 and Li_2 the next to lowest IP, corresponding to a different symmetry state of the ion than the ground state symmetry, can be calculated very accurately, several orders of magnitude more accurately than the next IP. But it is not quite as accurate as the lowest IP of the molecule. The question arises whether it is not as accurate because it is not exact, or whether the method of calculation has systematically excluded the basis functions needed to obtain more accurate calculations. In a previous calculation on Be [16] the basis set was partially optimized to obtain the best EKT IP into the second ^2P state of Be^+. This produced an accurate EKT IP into the lowest ^2P state of Be^+ and resulted in the conclusion that this EKT IP was exact. A systematic calculation of the same system resulted in the conclusion that it was not exact [15]. Whether or not these "other symmetry" lowest EKT IPs are exact, it appears that in some cases they can be obtained very accurately.

It is not clear whether the apparent inaccuracy of the EKT IPs is due to a fundamental theoretical limit or whether it is because in practical calculations the ill-conditioned nature of Eq. (1) precludes including natural orbitals with very small occupation numbers. It is likely that none of the natural orbital occupation numbers are identically zero for ground states of atoms and molecules [12]. If this is the case, one would expect that all of the EKT IPs would be exact and that the inaccuracies of the higher EKT IPs is due to omitting orbitals which are needed to obtain accurate ionization energies.

Acknowledgments

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