Complete-active-space extended Koopmans theorem method

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ABSTRACT

The complete-active-space (CAS) extended Koopmans theorem (EKT) method is defined as a special case of the EKT in which the reference state is a CAS configuration interaction (CI) expansion and the electron removal operator acts only on the active orbitals. With these restrictions, the EKT is equivalent to the CI procedure involving all hole-state configurations derived from the active space of the reference wavefunction and has properties analogous to those of the original Koopmans theorem. The equivalence is used to demonstrate in a transparent manner that the first ionization energy predicted by the EKT is in general not exact, i.e., not equal to the difference between the full CI energies of the neutral and the ion, but can approach the full CI result with arbitrary precision even within a finite basis set. The findings also reconcile various statements about the EKT found in the literature.

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The extended Koopmans theorem[1–5] (EKT) is a generalization of Koopmans's classic relation[6] between ionization energies and orbital eigenvalues to post-Hartree–Fock wavefunctions. The starting premise of the EKT is that the wavefunction for the kth state of the $(N - 1)$-electron ion can be approximated as a linear combination of hole-state configurations $\hat{a}_j \Psi^N$, where Ψ^N is a given normalized N-electron ground-state wavefunction and $\hat{a}_j$ are annihilation operators for the orthonormal spin-orbitals that lie in the space of the occupied natural orbitals of Ψ^N. Denoting this approximate wavefunction of the ion by $\tilde{\Psi}_k^{N-1}$, we write

$$\tilde{\Psi}_k^{N-1} = \hat{r}_k \Psi^N, \qquad (1)$$

where the operator

$$\hat{r}_k = \sum_j c_{jk} \hat{a}_j \qquad (2)$$

is the annihilator associated with a certain spin-orbital $r_k(\mathbf{x})$ whose removal from Ψ^N produces $\tilde{\Psi}_k^{N-1}$. To avoid symmetry problems for ion wavefunctions,[3] we assume throughout this work that Ψ^N describes a closed-shell system.

If $\hat{H}$ is a second-quantized Hamiltonian, then the energy of the N-electron system is

$$E^N = \langle \Psi^N | \hat{H} | \Psi^N \rangle \qquad (3)$$

and the energy of the kth state of the ion is

$$\tilde{E}_k^{N-1} = \langle \tilde{\Psi}_k^{N-1} | \hat{H} | \tilde{\Psi}_k^{N-1} \rangle, \qquad (4)$$

assuming that each $\tilde{\Psi}_k^{N-1}$ is normalized. We label the ion states by $k = 1, 2, \ldots$, so the ground state is $\tilde{\Psi}_1^{N-1}$.

A natural way to determine $\tilde{\Psi}_k^{N-1}$ and hence $\tilde{E}_k^{N-1}$ is by the configuration interaction (CI) method using the full set of the hole states $\hat{a}_j \Psi^N$. This approach, called hole-state CI (HCI), consists in making $\tilde{E}_k^{N-1}$ stationary with respect to variations of $\tilde{\Psi}_k^{N-1}$ subject to the constraint $\langle \tilde{\Psi}_k^{N-1} | \tilde{\Psi}_k^{N-1} \rangle = 1$ and amounts to the unconstrained optimization of the function

$$\tilde{E}_k^{N-1}(\mathbf{c}_k) = \frac{\langle \Psi^N | \hat{r}_k^\dagger \hat{H} \hat{r}_k | \Psi^N \rangle}{\langle \Psi^N | \hat{r}_k^\dagger \hat{r}_k | \Psi^N \rangle} = \frac{\mathbf{c}_k^\dagger \mathbf{H} \mathbf{c}_k}{\mathbf{c}_k^\dagger \mathbf{P} \mathbf{c}_k}, \qquad (5)$$

where $\mathbf{c}_k$ is a column vector of the expansion coefficients of $\hat{r}_k$,

$$H_{ij} = \langle \Psi^N | \hat{a}_i^\dagger \hat{H} \hat{a}_j | \Psi^N \rangle \qquad (6)$$

and

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

are elements of the one-electron reduced density matrix (1-RDM) for Ψ^N, $\rho(\mathbf{x}, \mathbf{x}')$. Optimization of Eq. (5) with respect to $\mathbf{c}_k$ leads to the matrix eigenvalue problem

$$\mathbf{H} \mathbf{c}_k = \tilde{E}_k^{N-1} \mathbf{P} \mathbf{c}_k. \qquad (8)$$

The kth ionization energy is then

$$I_k^{\text{HCI}} = \tilde{E}_k^{N-1} - E^N. \qquad (9)$$

However natural, equations (6)–(9) are *not* the EKT.

The original developers of the EKT considered but rejected[1] the HCI approach because it involves three-body operators $\hat{a}_i^\dagger \hat{H} \hat{a}_j$ and requires the 3-RDM to evaluate the matrix elements H_{ij}. To avoid this complication, they made an additional assumption that Ψ^N is a true eigenfunction of $\hat{H}$ so that

$$\langle \Psi^N | \hat{r}_k^\dagger \hat{r}_k \hat{H} | \Psi^N \rangle = E^N \langle \Psi^N | \hat{r}_k^\dagger \hat{r}_k | \Psi^N \rangle. \qquad (10)$$

By expressing E^N from Eq. (10) and subtracting the result from Eq. (5), Day *et al.*[1,2] obtained the expression

$$I_k^{\text{EKT}} = \frac{\langle \Psi^N | \hat{r}_k^\dagger [\hat{H}, \hat{r}_k] | \Psi^N \rangle}{\langle \Psi^N | \hat{r}_k^\dagger \hat{r}_k | \Psi^N \rangle}. \qquad (11)$$

Substitution of Eq. (2) into Eq. (11) and optimization of I_k^{EKT} (i.e., $\tilde{E}_k^{N-1}$ shifted by a constant E^N) with respect to $\mathbf{c}_k$ lead to the defining EKT equation,

$$\mathbf{K} \mathbf{c}_k = I_k^{\text{EKT}} \mathbf{P} \mathbf{c}_k, \qquad (12)$$

where $\mathbf{K}$ is the so-called Koopmans matrix[5] with the elements

$$K_{ij} = \langle \Psi^N | \hat{a}_i^\dagger [\hat{H}, \hat{a}_j] | \Psi^N \rangle \qquad (13)$$

whose evaluation requires the 2-RDM at most. Matrix $\mathbf{K}$ is Hermitian if Ψ^N is stationary with respect to spin-orbital variations within the space spanned by the occupied natural orbitals.[5] The negative of $\mathbf{K}$ is known as the generalized Fock matrix; this matrix also emerges in equation-of-motion[5,7,8] and electron propagator[9] techniques for evaluating electron binding energies.

Now, combination of Eqs. (5), (9), and (11) yields

$$I_k^{\text{HCI}} = I_k^{\text{EKT}} + \langle \Psi^N | \hat{r}_k^\dagger \hat{r}_k (\hat{H} - E^N) \Psi^N \rangle, \qquad (14)$$

which shows that the HCI and EKT become equivalent if the second term in Eq. (14) vanishes. Apart from the above-mentioned case of a true eigenfunction of $\hat{H}$, this also occurs for a Roothaan–Hartree–Fock wavefunction[10] in a finite (incomplete) basis set. The equivalence of the HCI and EKT results for the spin-restricted Hartree–Fock method was recently emphasized by Plakhutin and Davidson[11–13] as an alternative expression of the fact that the HCI expansion for a Hartree–Fock Ψ^N gives an ionization energy equal to the negative of the corresponding canonical orbital eigenvalue.

Are there other instances of equivalence of the EKT and HCI methods? This question brings us to our main point. An important class of post-Hartree–Fock wavefunctions includes complete active space (CAS) CI expansions $\Psi^N = \sum_J C_J \Phi_J^N$ in which configurations Φ_J^N contain the same doubly occupied core (inactive) orbitals and all permissible distributions of $p \leq N$ electrons among q spatial orbitals designated "active." The resulting space is labeled CAS(p, q). For CAS expansions with optimized CI coefficients, E^N is stationary with respect to variation of C_J, that is, $\langle \Phi_J^N | \hat{H} - E^N | \Psi^N \rangle = 0$.[5] This implies that

$$\langle \hat{a}_j^\dagger \hat{a}_i \Psi^N | \hat{H} - E^N | \Psi^N \rangle = \langle \Psi^N | \hat{a}_i^\dagger \hat{a}_j (\hat{H} - E^N) | \Psi^N \rangle = 0, \qquad (15)$$

provided both i and j refer to active spin-orbitals, because in that case, each $\hat{a}_j^\dagger \hat{a}_i \Psi^N$ is a linear combination of some configurations Φ_J^N. However, if Eq. (15) holds, then Eq. (10) is also satisfied. Thus, under the constraint that the operator $\hat{r}_k$ of Eq. (2) includes only annihilators for active spin-orbitals, the Koopmans matrix $\mathbf{K}$ for CAS-CI wavefunctions is Hermitian and the EKT applied to such wavefunctions (CAS-EKT for short) becomes equivalent to the HCI method, that is,

$$I_k^{\text{CAS-EKT}} = I_k^{\text{HCI}}. \qquad (16)$$

Full CI (FCI) expansions may be viewed as special cases of CAS-CI with zero core and zero virtual orbitals. For such expansions and for proper CAS-CI wavefunctions without core orbitals, the CAS EKT reduces to the conventional EKT method in which the domain of $\hat{r}_k$ is unrestricted.

The equivalence of the CAS-EKT and HCI methods permits one to analyze the properties of EKT solutions in a transparent way without any additional assumptions or reliance on precarious asymptotic arguments. For example, there is an extensive debate in the literature[14–25] on whether the EKT gives the first ionization energy exactly in the limit that Ψ^N is exact. To answer this question, we begin by extending the meaning of EKT exactness to approximate wavefunctions.

To be exact for a FCI wavefunction Ψ^N in a finite basis set, the EKT would have to produce I_1^{EKT} equal to

$$\Delta E_1^{\text{FCI}} = E_{1,\text{FCI}}^{N-1} - E^N, \qquad (17)$$

where $E_{1,\text{FCI}}^{N-1}$ is the ground-state FCI energy of the ion within the same basis set. We know that the EKT for FCI wavefunctions is equivalent to the HCI method. However, each HCI wavefunction $\tilde{\Psi}_1^{N-1}$ has an exact zero occupation number for the spin-orbital corresponding to the annihilated orbital, which means that the dimension of the space spanned by the spin-orbitals of $\tilde{\Psi}_1^{N-1}$ is lower than the dimension of the spin-orbital space of Ψ^N. Such a $\tilde{\Psi}_1^{N-1}$ cannot be the ion FCI wavefunction for $N > 2$ because, if it were, we would arrive at an absurd conclusion that any orthonormal basis set chosen for A is always larger than needed for A$^+$ and, in fact, for every ion A^{m+} ($1 \leq m \leq N - 2$) by at least m functions. For $N = 2$, this argument goes through because in that case, $\tilde{\Psi}_1^{N-1}$ is itself a spin-orbital and all but one of the natural occupation numbers are indeed zero. Thus, within FCI, the EKT is exact for $N = 2$ but not for $N > 2$.

To be exact for CAS(p, q) wavefunctions, the EKT would have to give the first ionization energy equal to

TABLE I. First EKT and CAS-CI ionization energies of Be calculated from ground-state CAS SCF and FCI wavefunctions using the cc-pCVXZ (X = D,T,Q,5) basis sets. All values are in atomic units (hartree).

X	E_{tot}[a]	I_1^{EKT}	$\Delta E_1^{\text{CAS−CI}}$	Defect[b]
	CAS(2,4)/cc-pCVXZ (pure)			
D	−14.615 452	0.348 521	0.349 400	−0.000 879
T	−14.616 531	0.348 932	0.349 723	−0.000 791
Q	−14.616 774	0.349 003	0.349 788	−0.000 785
5	−14.616 832	0.349 012	0.349 797	−0.000 785
	CAS(4,9)/cc-pCVXZ (pure)			
D	−14.649 430	0.348 522	0.348 398	0.000 124
T	−14.653 060	0.348 943	0.348 814	0.000 129
Q	−14.653 807	0.349 019	0.348 890	0.000 129
5	−14.653 897	0.349 028	0.348 899	0.000 129
	FCI/cc-pCVXZ (pure)			
D	−14.651 832	0.340 953	0.340 803	0.000 150
T	−14.662 366	0.341 923	0.341 883	0.000 040
Q	−14.665 680	0.342 411	0.342 395	0.000 016
5	−14.666 537	0.342 507	0.342 502	0.000 005
	FCI/basis-set limit from Ref. 26			
∞	−14.667 36		0.342 60	

[a] Total energy from the reference wavefunction. Convergence thresholds ACURCY and CVGTOL were adjusted as necessary to attain microhartree accuracy in the I_1^{EKT} values.
[b] Defect = $I_1^{\text{EKT}} − \Delta E_1^{\text{CAS−CI}}$.

$$\Delta E_1^{\text{CAS−CI}} = E_{1,\text{CAS−CI}}^{N−1} − E^N, \tag{18}$$

where $E_{1,\text{CAS−CI}}^{N−1}$ is the ground-state CAS$(p − 1, q)$-CI energy of A$^+$ evaluated using the CAS(p, q) spin-orbitals of A under the appropriate spin and symmetry restrictions. Since a CAS-CI expansion is generally larger than the corresponding HCI expansion, we have

$$I_1^{\text{CAS−EKT}} \geq \Delta E_1^{\text{CAS−CI}}, \tag{19}$$

where the strict equality holds for closed-shell CAS$(N, N/2)$ (Hartree–Fock) wavefunctions and for $N = 2$. Many excited CAS-CI states of A$^+$ will be missing from the HCI spectrum due to the absence of proper configurations.

To illustrate this analysis, we performed EKT calculations for various FCI and CAS self-consistent field (SCF) wavefunctions of the Be atom using the GAMESS (2020 R2) program.[27] Our results (Table I) and similar calculations reported in the literature[14,17,18,28–33] demonstrate that deviations of the EKT from exactness can be tantalizingly small. Note that the CAS(2,4) results in Table I violate Eq. (19). This is because conventional implementations of the EKT allow the annihilators $\hat{a}_j$ to act on core orbitals and involve more hole-state configurations than the CAS-EKT method.

Even though no removal orbital can yield the exact ion wavefunction for $N > 2$, Vanfleteren et al.[24] and Ernzerhof[25] showed that, for FCI wavefunctions, $\tilde{E}_1^{N−1}$ approaches the true $E_1^{N−1}$ in the basis-set limit. It turns out that $\tilde{E}_1^{N−1}$ can be arbitrarily close to $E_1^{N−1}$ even

TABLE II. Same properties as in Table I but using the cc-pCVDZ basis set supplemented with a nucleus-centered diffuse primitive function (s or d) with exponent α.

α	E_{tot}	I_1^{EKT}	$\Delta E_1^{\text{CAS−CI}}$	Defect
	CAS(4,9)/cc-pCVDZ+1s (pure)			
0.01	−14.649 442	0.348 521	0.348 397	0.000 124
0.005	−14.649 436	0.348 538	0.348 415	0.000 123
0.002	−14.649 432	0.348 530	0.348 407	0.000 123
0.001	−14.649 431	0.348 525	0.348 402	0.000 123
	FCI/cc-pCVDZ+1s (pure)			
0.01	−14.651 850	0.340 775	0.340 759	0.000 016
0.005	−14.651 841	0.340 795	0.340 786	0.000 009
0.002	−14.651 836	0.340 802	0.340 799	0.000 003
0.001	−14.651 834	0.340 803	0.340 802	0.000 001
	FCI/cc-pCVDZ+1d (Cartesian)			
0.01	−14.652 394	0.341 042	0.341 041	0.000 001
0.008	−14.652 392	0.341 045	0.341 045	$< 10^{−6}$

within finite-basis-set FCI, as we will now demonstrate by a similar argument.

Suppose we start with the same one-electron basis for A and A$^+$, supplement it with a diffuse (or remote) basis function $f(\mathbf{r})$ allowed by symmetry to contribute to the first EKT orbital $r_1(\mathbf{r})$, and use the expanded basis set to obtain ground-state FCI wavefunctions Ψ_{FCI}^N and $\Psi_{\text{FCI}}^{N−1}$. Because the exact wavefunction of A$^+$ decays faster than the exact wavefunction of A,[15] one can always make $f(\mathbf{r})$ so diffuse (or remote) that its contribution to $\Psi_{\text{FCI}}^{N−1}$ will be arbitrarily small relative to its contribution to Ψ^N, assuming that $f(\mathbf{r})$ dominates $r_1(\mathbf{r})$. However, if the removal of a basis function from Ψ^N can have an arbitrarily small effect on $\Psi_{\text{FCI}}^{N−1}$, then the EKT wavefunction $\tilde{\Psi}^{N−1}$ can be arbitrarily close to $\Psi_{\text{FCI}}^{N−1}$. This argument works for any $f(\mathbf{r})$ of proper symmetry, regardless of its asymptotic form.

Table II validates this prediction. Here, the cc-pCVDZ basis set for Be ([4s,3p,1d], $\alpha_{\min} = 0.0589$) is supplemented with a primitive diffuse s-type Gaussian $f_s(\mathbf{r}) \sim e^{−\alpha r^2}$ or with a set of six diffuse d-type Gaussians that contribute an s-type function of the form $f_s(\mathbf{r}) \sim r^2 e^{−\alpha r^2}$, which has a maximum at $r = \alpha^{−1/2}$. The supplemental function has little effect on the CAS(4,9) EKT results because it can contribute to $r_1(\mathbf{r})$ only through the nine active orbitals in which its role is small. The situation is very different for FCI wavefunctions, where $f_s(\mathbf{r})$ can contribute to $r_1(\mathbf{r})$ independently and significantly. As α decreases, I_1^{EKT} approaches ΔE_1^{FCI} and the relative weight of $f_s(\mathbf{r})$ in $r_1(\mathbf{r})$ increases, although other s-type basis functions still contribute appreciably even for $\alpha = 0.001$. The Mulliken population of $f_s(\mathbf{r})$, however, does decrease faster in $\Psi_{\text{FCI}}^{N−1}$ than in Ψ_{FCI}^N with decreasing α. Similar basis-set effects in FCI EKT calculations with a large basis set (cc-pV5Z) were reported in Ref. 24.

For Hartree–Fock wavefunctions, the CAS-EKT gives the same results as the ordinary Koopmans theorem: $I_k^{\text{EKT}} = −\epsilon_k$ and

$r_k(\mathbf{r}) = \psi_k(\mathbf{r})$, where $\psi_k(\mathbf{r})$ are the canonical orbitals and ϵ_k are their eigenvalues. In general, however, the first EKT removal orbital may bear little resemblance to the highest-occupied Hartree–Fock orbital (cf. Ref. 24).

The EKT removal orbitals should not be confused with Dyson spin-orbitals, which are defined by[34]

$$d_k = \sqrt{N}\langle \Psi_k^{N-1} | \Psi^N \rangle_{N-1}, \qquad (20)$$

where the ion wavefunctions Ψ_k^{N-1} are obtained independently from Ψ^N and the subscript after the ket indicates the number of electrons whose coordinates are integrated. Dyson orbitals differ from EKT orbitals in that $\langle d_k | \Psi^N \rangle_1 \neq \Psi_k^{N-1}$, $\langle d_k | \Psi_k^{N-1} \rangle_1 \neq 0$, and they are greater in number than $r_k(\mathbf{x})$. Nevertheless, one can use EKT wavefunctions to define approximate Dyson orbitals

$$g_k = \sqrt{N}\langle \breve{\Psi}_k^{N-1} | \Psi^N \rangle_{N-1} \qquad (21)$$

that are similar to the true Dyson orbitals for lower-energy states.[35] The number of g_k orbitals is equal to the number of the EKT orbitals r_k. Substituting Eq. (2) into Eq. (21), we see that $g_k(\mathbf{x})$ and $r_k(\mathbf{x})$ are related by

$$g_k(\mathbf{x}) = \int \rho(\mathbf{x}, \mathbf{x}') r_k(\mathbf{x}') \, d\mathbf{x}', \qquad (22)$$

where $\rho(\mathbf{x}, \mathbf{x}')$ is the 1-RDM derived from Ψ^N. If the last equation is multiplied by the natural spin-orbital $\phi_j^*(\mathbf{x})$ and integrated, one obtains the relation

$$\langle \phi_j | r_k \rangle = n_j^{-1} \langle \phi_j | g_k \rangle, \qquad (23)$$

which shows that natural orbitals with small occupation numbers can make large contributions to EKT orbitals.

The CAS-EKT approach instantly settles another question: Are EKT outputs well-defined for reference wavefunctions with very small natural orbital occupation numbers? The issue here is that Eq. (12) is usually solved[28] through symmetric orthogonalization using the matrix $\mathbf{P}^{-1/2}$, which is almost singular if at least one n_k is close to zero. The answer is affirmative because the I_k^{EKT} spectrum is just the well-defined HCI eigenvalue spectrum shifted by E^N.

In summary, we have shown that the EKT applied to CAS-CI wavefunctions is equivalent to the hole-space CI method if the electron removal operator $\hat{r}$ is restricted to the active space. This equivalence implies that, within FCI, the first EKT ionization energy, I_1^{EKT}, cannot be exactly equal to the difference between the FCI energies of the N-electron system ($N > 2$) and the corresponding cation, ΔE_1^{FCI}. Previous workers[24,25] concluded that I_1^{EKT} approaches ΔE_1^{FCI} in the limit that the reference wavefunction Ψ^N is an exact solution of the Schrödinger equation. The CAS-EKT method yields a stronger result: For FCI wavefunctions, I_1^{EKT} can be arbitrarily close to ΔE_1^{FCI} even within an incomplete (finite) basis set, provided that this set contains a function that contributes to Ψ^{N-1} much less than to Ψ^N. The exactness of the EKT does not hinge on the asymptotic properties of Ψ^N, which is consistent with recent findings[36,37] that the first ionization energy can be extracted from the long-range behavior of Gaussian-basis-set molecular wavefunctions even though they do not exhibit the exponential asymptotic decay.[4,15]

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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