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Uncorrelated (Hartree–Fock) *ab initio* calculations have proven unable to predict the energy ordering of $3\sigma_g$ and $1\pi_u$ molecular orbitals as observed in electron spectroscopy experiments on fluorine (F_2). The correct ordering was obtained, however, by applying an extension of Koopmans' theorem [J. Chem. Phys. **62**, 113 (1975)] to an MC–SCF correlated wavefunction for F_2 which contained only one configuration beyond the one used in Hartree–Fock. With the addition of still further configurations to the wavefunction for the neutral molecule, the ordering of the extended Koopmans' valence orbital energies was maintained and the correspondence improved between those and the experimental values.

INTRODUCTION

Molecular fluorine F_2 is one of the best-known systems for which Koopmans' theorem[1] (KT) breaks down. Orbital energies from single configuration (Hartree–Fock) *ab initio* calculations[2] have proven unable to predict the energy ordering of its valence σ_g and π_u molecular orbitals as inferred from electron spectroscopy experiments.[3,4] But in a calculation recently performed in our laboratory, the correct ordering was obtained by applying an extension[5,6] of KT to a two configuration self-consistent-field wavefunction[7] for ground-state neutral $F_2[X^1\Sigma_g^+]$, Eq. (1) with $R = 2$.

Application of this extended Koopmans' theorem (EKT) to F_2 multiconfiguration–self-consistent-field (MC–SCF) wavefunctions which included still more doubly excited configurations,[7] $R = 4$ and $R = 6$ in Eq. (1), maintained the correct ordering and improved the correspondence between the values of the extended Koopmans' valence orbital energies and those inferred from experiment[3] (see Table III). The 18-electron configurations $\Phi_K^{(18)}$ ($K = 1, 2, \ldots, R$) for each self-consistent F_2 ground-state wavefunction $\Psi_{R\text{conf}}^{(18)}$ were taken from the set shown in Eqs. (2):

$$\Psi_{R\text{conf}}^{(18)}[F_2(X^1\Sigma_g^+)] = \sum_{K=1}^R A_K \Phi_K^{(18)}, \tag{1}$$

$$\Phi_1^{(18)} = |(\text{core})1\pi_u^4 1\pi_g^4 3\sigma_g^2\rangle, \tag{2a}$$

$$\Phi_2^{(18)} = |(\text{core})1\pi_u^4 1\pi_g^4 3\sigma_u^2\rangle, \tag{2b}$$

$$\Phi_3^{(18)} = |(\text{core})1\pi_u^2 1\pi_g^4 3\sigma_g^2 3\sigma_u^2\rangle, \tag{2c}$$

$$\Phi_4^{(18)} = |(\text{core})1\pi_u^4 1\pi_g^2 3\sigma_g^2 3\sigma_u^2\rangle, \tag{2d}$$

$$\Phi_5^{(18)} = |(\text{core})1\pi_u^3 1\pi_g^4 3\sigma_g 3\sigma_u 2\pi_g\rangle, \tag{2e}$$

$$\Phi_6^{(18)} = |(\text{core})1\pi_u^4 1\pi_g^3 3\sigma_g 3\sigma_u 2\pi_u\rangle, \tag{2f}$$

where

$$(\text{core}) \equiv (1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2). \tag{2g}$$

THE EXTENDED KOOPMANS' THEOREM AND THE MC–SCF METHOD

We shall briefly explain the manner in which EKT, which applies to configuration interaction (CI) wave-

functions, is particularly suited for the determination of approximate ionic states and ionization potentials (I. P.'s) for neutral systems which are to be represented by MC–SCF[8] wavefunctions.

We first write the N-electron molecular Hamiltonian H as a sum of one- and two-electron terms and define the well-known first and second order reduced density matrices[9] $\gamma(x_1 | x_1')$ and $\Gamma(x_1 x_2 | x_1' x_2')$, respectively:

$$H(x_1 x_2 \cdots x_N) = \sum_{i=1}^N h(x_i) + \sum_i \sum_{i<j} g(x_i, x_j), \tag{3}$$

$$\Gamma(x_1 x_2 | x_1' x_2') = \binom{N}{2} \int \Psi^{(N)}(x_1 x_2 x_3 \cdots x_N)$$
$$\times \Psi^{(N)*}(x_1' x_2' x_3 \cdots x_N) dx_3 \cdots dx_N, \tag{4}$$

$$\gamma(x_1 | x_1') = N \int \Psi^{(N)}(x_1 x_2 x_3 \cdots x_N)$$
$$\times \Psi^{(N)*}(x_1' x_2 x_3 \cdots x_N) dx_2 dx_3 \cdots dx_N. \tag{5}$$

The latter two operators may be expanded in a basis set of orthonormal spin orbitals

$$\left\{ \psi_k(x) \,\middle|\, \int \psi_i^* \psi_j \, dx = \delta_{ij} \right\},$$

$$\Gamma(x_1 x_2 | x_1' x_2') = \sum_i \sum_j \sum_k \sum_l \psi_i(x_1) \psi_j(x_2) \Gamma_{ijkl} \psi_k^*(x_1') \psi_l^*(x_2'), \tag{4a}$$

$$\gamma(x_1 | x_1') = \sum_i \sum_j \psi_i(x_1) \gamma_{ij} \psi_j^*(x_1'). \tag{5a}$$

The MC–SCF method is frequently used for the determination of an M-dimensional orthonormal spin-orbital basis set $\{\psi_k\}$ in N-electron CI wavefunctions of the form

$$\Psi^{(N)} = \sum_K A_K \Phi_K^{(N)}. \tag{6}$$

Configurations $\Phi_K^{(N)}$ are symmetry adapted linear combinations of determinantal functions

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$$\Phi_K^{(N)} = \sum_v \Theta_v \det[\psi_{i_1}^{Kv}(1)\psi_{i_2}^{Kv}(2)\cdots\psi_{i_N}^{Kv}(N)] \ .$$

During the course of an MC–SCF calculation, Eqs. (7) must be solved iteratively for the orbitals until the self-consistency condition (8) on Lagrange multipliers λ_{ji} has been satisfied:

$$\sum_{j=1}^{M} \hat{F}_{ij}(x)\psi_j(x) = \sum_{j=1}^{M} \psi_j(x)\lambda_{ji} \ , \tag{7}$$

$$\lambda_{ji} = \lambda_{ij}^* \ . \tag{8}$$

The λ_{ji} are determined by an equation of the form

$$\lambda_{ji} = \sum_{k=1}^{M} \int \psi_j^*(x)\hat{F}_{ik}(x)\psi_k(x)\,dx = \sum_{k=1}^{M} \int \psi_j^*(x)\left[h(x)\gamma_{ki} + 2\sum_l \sum_m \int \psi_m^*(x'')g(x,x'')\psi_l(x'')\,dx''\,\Gamma_{lmki}\right]\psi_k(x)\,dx$$

$$= \sum_{k=1}^{M}\sum_{n=1}^{M} \int \psi_j^*(x)\left[h(x)\gamma_{kn} + 2\sum_l \sum_m \int \psi_m^*(x'')g(x,x'')\psi_l(x'')\,dx''\,\Gamma_{lmkn}\int\psi_n^*(x')\psi_i(x')\,dx'\right]\psi_k(x)\,dx \ . \tag{9}$$

By substituting expansions (4a) and (5a) into (9), it may be seen that the Hermitian matrix λ is the representation of the extended Hartree–Fock nonlocal potential[9,10] $V^<(x,x')$ within the self-consistent MC–SCF basis

$$\lambda_{ji} = \iint \psi_j^*(x)V^<(x,x')\psi_i(x')\,dx\,dx' \ , \tag{10}$$

$$V^<(x,x') = h(x)\gamma(x,x') + 2\int g(x,x'')\Gamma(x'',x|x'',x')\,dx'' \ . \tag{11}$$

Day, Smith, and Garrod[11] demonstrated that diagonalizing this potential with respect to metric γ in the secular equations (12) determines variational approximations $\widetilde{\text{I.P.}}_{\cdot k}$ and $\widetilde{\Psi}_k^{(N-1)}$ to exact I.P.'s and exact positive ionic states of the system described by $\Psi^{(N)}$:

$$(\lambda - \gamma\epsilon)\mathbf{C} = 0 \ , \tag{12}$$

$$\widetilde{\text{I.P.}}_{\cdot k} \equiv -\epsilon_k \ , \tag{13}$$

$$\widetilde{\Psi}_k^{(N-1)} \equiv \int \chi_k^*(x_N)\Psi^{(N)}(x_1,x_2,\cdots,x_N) \ , \tag{14}$$

where

$$\chi_k(x) = \sum_{j=1}^{M} \psi_j(x)C_{jk} \ . \tag{15}$$

$\widetilde{\Psi}_k^{(N-1)}$ will be variationally stable within the space spanned by $\{\Psi_j^{(N-1)} \equiv \int \psi_j^*(x_N)\Psi^{(N)}\,dx_N \mid j = 1, \cdots, M\}$, where ψ_j is any one of the self-consistent spin orbitals employed in the minimum energy N-particle wavefunction $\Psi^{(N)}$. The one-particle functions χ_k are termed natural transition orbitals (NTO's).

From Eq. (10), λ may easily be calculated and used to find I.P.'s for multiconfiguration states $\Psi^{(N)}$ determined by an ordinary noniterative CI procedure if $\Psi^{(N)}$ is a full CI function over the spin–orbital basis. Several atomic calculations of this type have been published. But when λ is computed from partial CI expansions over orbitals which have not been optimized in the MC–SCF process the matrix will not, in general, be Hermitian. We have discovered that trying to compensate for this by simply taking the Hermitian component of λ, $\frac{1}{2}(\lambda^\dagger + \lambda)$, gives less than satisfactory results because then the energies of the ionic states $\widetilde{\Psi}_k^{(N-1)}$ are no longer variationally determined.[5]

Fortunately, for multiconfiguration wavefunctions arising from the self-consistent solutions to Eq. (7), λ must, by Eq. (8), be Hermitian.

The variational procedure implicit in the solution of Eq. (12) constitutes an extension of Koopmans' theorem to correlated wavefunctions.[5,6] EKT in the MC–SCF formalism is the precise mathematical analog of KT in the (Hartree–Fock) self-consistent field (SCF) formalism. Just as the MC–SCF equations reduce to the ordinary SCF equations, so this extension of KT reduces to the original KT in the special case that $\Psi^{(N)}$ is a single configuration.[11]

THE KOOPMANS' THEOREM ANOMALY FOR F_2

Wahl[2] used the SCF method to variationally optimize a large analytic single determinant wavefunction of the form (2a) for F_2. A total energy of $E_{SCF} = -198.7683$ hartree was calculated at the equilibrium internuclear distance of 2.68 bohr (Tables I and II). This was presumed to be close to the Hartree–Fock limit. The orbital energies Wahl found for each of the molecular orbitals in the determinant are listed in line 1 of Table III. As shown in Table III and Fig. 1, the KT orbital energies predict an energy ordering for the $3\sigma_g$ and $1\pi_u$ molecular orbitals which does not correspond with the experimental inference from electron spectroscopy that $-\epsilon(3\sigma_g) > -\epsilon(1\pi_u)$. [Here, $\epsilon(k) \equiv \epsilon_k$.]

Koopmans' theorem produces similarly anomalous results when applied to a near Hartree–Fock SCF wavefunction for molecular nitrogen N_2. In fact, for F_2 and N_2, even separate SCF calculations on each ionic state do not yield the right order.[12,13] Such anomalies in KT results have been attributed[4,12,14,15] to the inherent weakness of the Hartree–Fock model: that it does not account for electron correlation. By definition,[16] the energy due to correlation is that which is neglected in this approximation to the exact nonrelativistic energy

$$E_{SCF} = E_{exact} - E_{corr} \ .$$

Hence, Koopmans' original method cannot claim a constant error in its estimate of the energies for the neutral and ionic states. The approximate wavefunctions for the two states are equally "uncorrelated," but real systems with N and $(N-1)$ electrons have different amounts of correlation energy contributing to the energy difference. Further, when an electron is removed from an N-electron determinant following the Koopmans' prescription, no reorganization of the remaining

TABLE I. Coefficients for normalized configurations in the several $F_2[X^1\Sigma_g^+]$ wavefunctions [a] at $R_e = 2.68$ bohr.

Wavefunction	A_1	A_2	A_3	A_4	A_5	A_6
$\Phi_1^{(18)\ Wahl}$ [b]	1.0	0.0	0.0	0.0	0.0	0.0
$\Phi_1^{(18)}$ [c]	1.0	0.0	0.0	0.0	0.0	0.0
$\Psi_{2conf}^{(18)}$ [c]	0.96740	−0.25325	0.0	0.0	0.0	0.0
$\Psi_{4conf}^{(18)}$ [c]	0.96686	−0.25058	0.01570	0.04623	0.0	0.0
$\Psi_{6conf}^{(18)}$ [c]	0.97191	−0.19575	0.01761	0.04897	−0.05605	−0.10595

[a]All configurations in MC−SCF wavefunctions $\Psi_{2conf}^{(18)}$, $\Psi_{4conf}^{(18)}$, and $\Psi_{6conf}^{(18)}$ are expressed over an expansion set of Slater-type orbitals described in Ref. 7(a). The larger expansion set for the SCF single configurations $\Phi_1^{(18)\ Wahl}$ and $\Phi_1^{(18)}$ is given in Ref. 2.
[b]As calculated by Wahl, Ref. 2.
[c]Wavefunction recalculated for this work.

$(N-1)$ electrons take place in the single determinant which represents the ionic state produced.

Elaborate schemes which apply perturbation theory and one-particle Green's functions to the N-electron Hartree−Fock reference state have been devised in efforts to remedy these difficulties, especially in the cases of F_2 and N_2. [4,15,17]

Of course, a rigorous (and expensive) means to theoretically determine the F_2 valence ionization potentials is to perform a separate CI calculation on each ionic state. Minimal basis set calculations of this type can yield the observed order of the ionic states even when the total energies of the CI wavefunctions are well above the Hartree−Fock limit. [18]

EXTENDED KOOPMANS' CALCULATIONS ON F_2

It was one objective of this work to see if EKT would resolve the Koopmans' anomaly for F_2 without solving Schrödinger's equation twice. Using a multiconfiguration wavefunction to account for correlation, it was our hypothesis that sufficient many-body effects would auto-

matically be embodied in the NTO's χ_k, and the orbital energies ϵ_k to obtain the experimentally inferred ordering of ionic states from EKT.

Molecular fluorine was chosen as the test case in our work, rather than N_2 where an analogous breakdown of KT occurs, because a series of MC−SCF wavefunctions for F_2 had been described in the literature in great detail by Das and Wahl. [7] In earlier work, [2] Wahl's analytic single determinant wavefunction over a large basis set for F_2 had failed to give a positive binding energy with respect to the Hartree−Fock atoms. He attributed this to an inherent defect of single determinant states. They neglect a major contribution to the binding, the correlation energy, which is greater in F_2 than in the separated F atoms. The cause of the negative binding energies is analogous to the cause of the aforementioned difficulties with Koopmans' theorem for the F_2 molecule: failure of the single-determinant SCF method to correlate different states differently. Das and Wahl discovered that the addition of only one (the next most dominant) excited MC−SCF configuration accounted for sufficient correlation $E_{corr} = 0.07500$ hartree

TABLE II. Total energies (E_T), correlation energies (E_{corr}), and dissociation energies (D_e) in hartrees [a] for the several $F_2[X^1\Sigma_g^+]$ wavefunctions at $R_e = 2.68$ bohr.

Wavefunction	E_T	E_{corr}	$\% E_{corr}^{(exptl)}$	D_e	$\% D_e^{(exptl)}$
$\Phi_1^{(18)\ Wahl}$ [f]	−198.76825	0.00	0.00	−0.04959 [c]	···
$\Phi_1^{(18)}$ [g]	−198.76822	−0.00003	···	−0.04962 [c]	···
$\Psi_{2conf}^{(18)}$ [g]	−198.8371	0.0688	7.6	0.0189 [d]	30.6
$\Psi_{4conf}^{(18)}$ [g]	−198.83899	0.0707	7.8	0.0208 [d]	33.7
$\Psi_{6conf}^{(18)}$ [g]	−198.87768	0.1094	12.1	0.0595 [d]	96.4
Exptl.	−199.670 [b]	0.902	100.0	0.0617 [e]	100.0

[a]1 hartree = 27.2107 eV.
[b]As quoted in Ref. 7(c).
[c]Energy of dissociated Hartree−Fock F atoms from the calculation by Bagus and Gilbert as quoted in Ref. 7(c). $E(R = \infty) = -198.81784$ hartree.
[d]Energy of dissociated MC−SCF F atoms from six-configuration calculation at $R = 6.00$ bohr in Ref. 7(a). $E(R = 6.0$ bohr$) = -198.8182$ hartree.
[e]As quoted in Ref. 7(a).
[f]As calculated by Wahl, Ref. 2.
[g]Wavefunction recalculated for this work.

TABLE III. Comparison of ionization potentials[a] for F_2 at $R = 2.68$ bohr determined from Koopmans' theorem (KT), extended Koopmans' theorem (EKT), and experiment.

Source	Core orbitals				Valence orbitals			Correlation orbitals		
	$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$2\sigma_u$	$1\pi_u$	$1\pi_g$	$3\sigma_g$	$3\sigma_u$	$2\sigma_u$	$2\sigma_g$
KT; $\Phi_1^{(18)\,Wahl}$ [b]	26.42269	26.42244	1.75654	1.49499	0.80523	0.66290	0.74604	...	...	...
KT; $\Phi_1^{(18)}$ [c]	26.4223	26.4220	1.7564	1.4949	0.8051	0.6628	0.7459	...	...	...
EKT; $\Psi_{2conf}^{(18)}$ [c]	26.3964	26.3961	1.7435	1.4821	0.7933	0.6505	0.8146	1.2433	...	...
EKT; $\Psi_{4conf}^{(18)}$ [c]	26.3961	26.3959	1.7433	1.4873	0.7931	0.6511	0.8129	1.2543	...	...
EKT; $\Psi_{6conf}^{(18)}$ [c]	26.4023	26.4021	1.7462	1.4812	0.7860	0.6563	0.8387	2.1903	4.1720	4.8206
Exptl. [d]					0.691	0.582	0.772			

[a]Energies in hartrees. 1 hartree = 27.2107 eV.
[b]Reference 2.
[c]This work.
[d]Reference 3.

to achieve a positive binding energy of $D_e = 0.02505$ hartree. A six-configuration MC–SCF wavefunction improved that figure to $D_e = 0.06706$ hartree. The expansion set of Slater-type orbitals used for the MC–SCF wavefunctions was a subset of the one used in Wahl's single determinant.

Since the small MC–SCF wavefunctions included sufficient many-body effects to bind F_2, it seemed probable that they might also suffice to correctly predict the order of valence ionizations by way of EKT.

We recalculated the Das and Wahl two-, four-, and six-configuration wavefunctions [Eq. (1) with $R = 2, 4, 6$] using the BISON and BISON–MC programs written at the Argonne National Laboratory.[19] Applying EKT to these wavefunctions, we were able in all three cases to calculate orbital energies for F_2 having the experimentally inferred order. Our results appear in columns 3 through 5 of Table II. These are the first extended Koopmans' calculations to be made using *ab initio* molecular wavefunctions as input.

Solution of Eq. (12) to obtain all the extended Koopmans' orbital energies listed in Table III was accomplished in only a few seconds of computer time. Since calculation of the MC–SCF ground state wavefunctions required an investment of nearly two hours of central processor time on an IBM 370/model 58 computer, it is not unreasonable to assert that all the information about the ion is then gotten virtually for free.

In Fig. 1 are plotted on the same energy scale the various sets of results for the valence ionization potentials in question. At the right of the figure experimental values inferred from electron spectroscopy indicate that it should be more difficult to ionize an electron from the $3\sigma_g$ molecular orbital (MO) than from the $1\pi_u$ molecular orbital. But at the extreme left KT results from the SCF single configuration predict just the opposite. Moving right, the two-configuration EKT results correspond with the experimental energy ordering as a consequence of a large increase in the absolute magnitude of the $3\sigma_g$ orbital energy and a slight decrease in that for $1\pi_u$.

The valence orbital energies obtained from the four- and six-configuration wavefunction by EKT maintain the

correspondence with the experimental order, and the differences between the orbital energies from the latter wavefunction show remarkably good agreement with experiment, although the absolute magnitudes of these calculated I. P.'s are all too large by between 0.06 and 0.09 hartree.

Since no core excitations are included in any of the MC–SCF wavefunctions described here, the core orbital energies obtained from EKT are essentially the same as those from KT. Pickup[20] has used one-particle propagators to perform an analysis of the extended Koopmans' theorem. His conclusion that it should prove useful for describing valence ionization processes, but less useful for core ionizations, is in accord with the results of previously published atomic EKT calculations and those contained in this paper, as well. EKT ionization potentials for the F_2 correlation orbitals
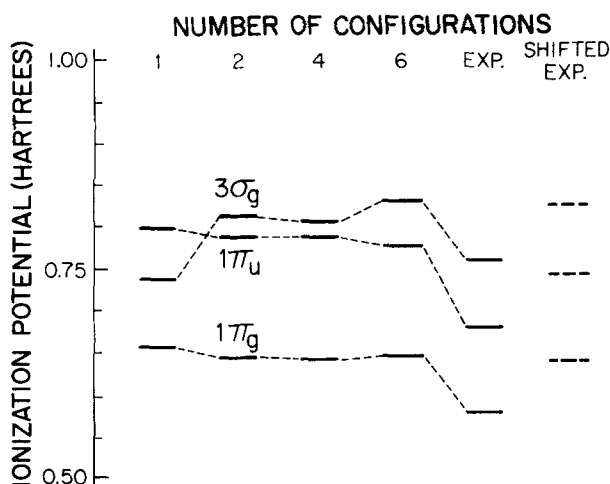

FIG. 1. F_2 valence ionization potentials (V.I.P.'s) from a single configuration via Koopmans' theorem, from multiconfiguration wavefunctions via the extended Koopmans' theorem, and from experiment. See also Table III. Spacings of experimental V.I.P.'s are compared with best theoretical spacings in the rightmost column of the figure, which plots all experimental V.I.P.'s shifted upward by an amount such that the lowest shifted experimental V.I.P. equals the lowest V.I.P. from a six-configuration wavefunction.

TABLE IV. Orthonormal[a] natural transition orbitals (NTO's) $\chi_i^\dagger = \Sigma_k \psi_k c_{ki}^\dagger$ from F_2 MC–SCF wavefunctions.

	k	$\chi^\perp(1\sigma_g)$	$\chi^\perp(1\sigma_u)$	$\chi^\perp(2\sigma_g)$	$\chi^\perp(2\sigma_u)$	$\chi^\perp(1\pi_u)$	$\chi^\perp(1\pi_g)$	$\chi^\perp(3\sigma_g)$	$\chi^\perp(3\sigma_u)$	$\chi^\perp(2\pi_u)$	$\chi^\perp(2\pi_g)$
From $\Psi_{2conf}^{(18)}$	1	1.000000	0.000000	−0.000081	0.000000	0.000000	0.000000	0.000085	0.000000		
	2	0.000000	0.999999	0.000000	0.001003	0.000000	0.000000	0.000000	0.000349		
	3	0.000082	0.000000	0.999971	0.000000	0.000000	0.000000	−0.007554	0.000000		
	4	0.000000	−0.001045	0.000000	0.988010	0.000000	0.000000	0.000000	0.154389		
	5	0.000000	0.000000	0.000000	0.000000	1.000000	0.000000	0.000000	0.000000		
	6	0.000000	0.000000	0.000000	0.000000	0.000000	1.000000	0.000000	0.000000		
	7	−0.000085	0.000000	0.007554	0.000000	0.000000	0.000000	0.999971	0.000000		
	8	0.000000	−0.000190	0.000000	−0.154389	0.000000	0.000000	0.000000	0.988010		
From $\Psi_{4conf}^{(18)}$	1	1.000000	0.000000	−0.000081	0.000000	0.000000	0.000000	0.000085	0.000000		
	2	0.000000	0.999999	0.000000	0.001009	0.000000	0.000000	0.000000	0.000315		
	3	0.000082	0.000000	0.999972	0.000000	0.000000	0.000000	−0.007541	0.000000		
	4	0.000000	−0.001045	0.000000	0.988348	0.000000	0.000000	0.000000	0.152205		
	5	0.000000	0.000000	0.000000	0.000000	1.000000	0.000000	0.000000	0.000000		
	6	0.000000	0.000000	0.000000	0.000000	0.000000	1.000000	0.000000	0.000000		
	7	−0.000084	0.000000	0.007541	0.000000	0.000000	0.000000	0.999972	0.000000		
	8	0.000000	−0.000157	0.000000	−0.152205	0.000000	0.000000	0.000000	0.988349		
From $\Psi_{6conf}^{(18)}$	1	1.000000	0.000000	−0.000073	0.000000	0.000000	0.000000	0.000103	0.000000	0.000000	0.000000
	2	0.000000	0.999999	0.000000	0.001065	0.000000	0.000000	0.000000	0.000024	0.000000	0.000000
	3	0.000073	0.000000	0.999970	0.000000	0.000000	0.000000	−0.007759	0.000000	0.000000	0.000000
	4	0.000000	−0.001061	0.000000	0.997472	0.000000	0.000000	0.000000	−0.071053	0.000000	0.000000
	5	0.000000	0.000000	0.000000	0.000000	0.997915	0.000000	0.000000	0.000000	0.064548	0.000000
	6	0.000000	0.000000	0.000000	0.000000	0.000000	0.998582	0.000000	0.000000	0.000000	0.053244
	7	−0.000103	0.000000	0.007759	0.000000	0.000000	0.000000	0.999970	0.000000	0.000000	0.000000
	8	0.000000	−0.000099	0.000000	0.071053	0.000000	0.000000	0.000000	0.997473	0.000000	0.000000
	9	0.000000	0.000000	0.000000	0.000000	−0.064548	0.000000	0.000000	0.000000	0.997915	0.000000
	10	0.000000	0.000000	0.000000	0.000000	0.000000	−0.053244	0.000000	0.000000	0.000000	0.998582

[a]If ψ_k is an MC–SCF spinorbital, C are the eigenvectors of text Eq. (12), and γ is the 1-matrix, then nonorthonormal NTO's are written $\chi_i = \Sigma_k \psi_k c_{ki}$ and $C^\dagger \gamma C = 1$. Solving $(\gamma - 1n)W = 0$, orthonormal NTO's are $\chi_i^\dagger = \Sigma_k \Sigma_l \psi_k n_k^{1/2} W_{kl} c_{li} = \Sigma_k \psi_k c_{ki}^\dagger$.

correspond to "shake-up" states.[5,6] (See note added in proof.)

DISCUSSION

A simple explanation for the two-configuration EKT result (and, by implication, the F_2 Koopmans' anomaly) can be given by examining the $^2\Sigma_g^+$ and $^2\Pi_u$ ionic states generated from $\Psi_{2conf}^{(18)}$ by EKT and comparing them to ionic states of the same symmetries generated from $\Phi_1^{(18)}$ by KT. Referring to Table IV, we write

$$\chi(3\sigma_g) \approx \psi(3\sigma_g) \tag{16a}$$

$$\chi(1\pi_u) \approx \psi(1\pi_u) , \tag{16b}$$

where the ψ are orthonormal MC–SCF spin orbitals and the χ are defined by Eq. (15). [Here, $\psi(k) \equiv \psi_k$ and $\chi(k) \equiv \chi_k$.] Then, from Eqs. (1), (2), (5) and (14), the two EKT ionic states are

$$^2\Sigma_g^+ : \bar\Psi^{(17)}(3\sigma_g) \approx \int \psi^*(3\sigma_g)\Psi_{2conf}^{(18)} dx_{18} = |(\text{core}) 1\pi_u^4 1\pi_g^4 3\sigma_g\rangle , \tag{17a}$$

$$^2\Pi_u : \bar\Psi^{(17)}(1\pi_u) \approx \int \psi^*(1\pi_u)\Psi_{2conf}^{(18)} dx_{18}$$
$$= A_1|(\text{core}) 1\pi_u^3 1\pi_g^4 3\sigma_g^2\rangle + A_2|(\text{core})1\pi_u^3 1\pi_g^4 3\sigma_u^2\rangle . \tag{17b}$$

By using KT we would obtain a $^2\Sigma_g^+$ ionic state $\Phi_1^{(17)}(3\sigma_g)$ of the same form as Eq. (17a) and very close to it in total energy. On the other hand, KT represents the cation by only the (renormalized) first term of Eq. (17b), which cannot be as low in total energy as $\Psi^{(17)}(1\pi_u)$. Finally, we note that because of configuration interaction, $\Psi_{2conf}^{(18)}$ is lower in energy than the SCF ground neutral state $\Phi_1^{(18)}$.

The situation described in the preceding paragraph is depicted in Fig. 2. From the schematic representation of the one- and two-configuration results in Fig. 2 and the scale drawing of them in Fig. 1, two things may be observed: (1) The increase in $-\epsilon(3\sigma_g)$, about 0.07 hartree, is almost entirely due to the effect of configuration interaction in the neutral state where E_{corr}
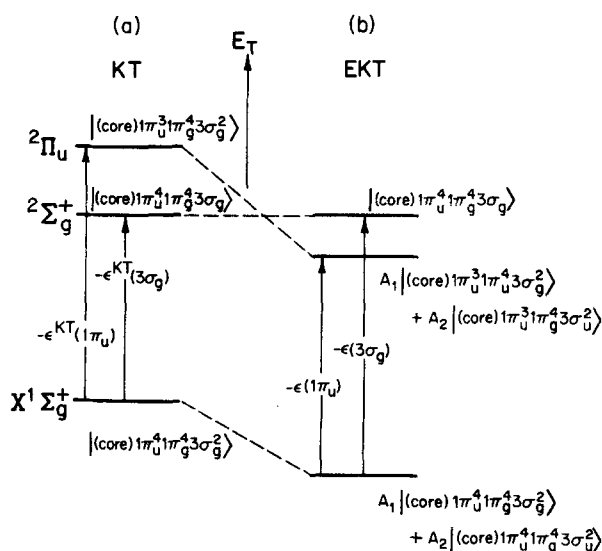

FIG. 2. Schematic explanation of the correction of Koopmans' anomaly by EKT. (a) Anomalous ordering of F_2 ionic states according to KT; and (b) correct ordering according to EKT because total energies (E_T) of neutral $X^1\Sigma_g^+$ and ionic $^2\Pi_u$ states are lowered via configuration interaction, while the energy of the $^2\Sigma_g^+$ cation remains relatively unchanged. (See text. Also compare Fig. 2 with results in Fig. 1 and Table III.)

= 0.075 hartree; (2) the first excited configuration lowers the energy in the $^2\Pi_u$ ion even more than in the $X^1\Sigma_g^+$ neutral, where $3\sigma_g^2 \rightarrow 3\sigma_u^2$ represents the principal correlation effect. The combination of these two effects causes the crossover of the energy states to give the correct order in going from the one- to the two-configuration results.

Simply stated, the Koopmans' anomaly for F_2 occurs because with a single configuration KT represents the $^2\Sigma_g^+$ cation relatively more accurately than the $^2\Pi_u$ cation.

Reasoning similar to that detailed above may be used to analyze the four- and six-configuration EKT results. In general, an orbital energy in Fig. 1 rises when additional configurations introduce less correlation energy into the corresponding ion than the "parent" neutral state. An orbital energy falls when the reverse is true.

Naturally, terms beyond the sixth in the CI expansion will have smaller coefficients and smaller individual energy effects than those already included. It seems unlikely that any combination of additional configurations would mix so much more strongly in $\Psi^{(17)}(3\sigma_g)$ than in $\Psi^{(17)}(1\pi_u)$ as to put the EKT $^2\Sigma_g^+$ and $^2\Pi_u$ states in the wrong energy order. However, EKT I. P.'s for larger F_2 MC–SCF wavefunctions are being investigated to confirm this prediction and possibly improve upon the six-configuration result.

Extended Koopmans' calculations from MC–SCF wavefunctions for molecular nitrogen and other first row diatomic molecules are also planned.

CONCLUSIONS

Despite the deceptively straightforward mathematical analogy that can be drawn between EKT and KT, an important conceptual innovation is implicit in the extension of Koopmans' theorem to multiconfiguration wavefunctions. Such wavefunctions, unlike Hartree–Fock states, explicitly take into account many-body effects in more than an average way. As a result, the NTO's generated by EKT, though they are only one-particle functions, must also incorporate some many-body effects.

The concept of one-particle functions is at the heart of almost all models in quantum chemistry. But, heretofore, many such one-particle models had been restricted to mathematical descriptions based upon the Hartree–Fock, which neglects or averages out many-body effects. The notion of one-particle building blocks for true many-body molecular states as advanced by EKT broadens the realm of the one-particle model for molecules and enhances its usefulness.

Koopmans' theorem fails to correctly order the ionic states of F_2 because the canonical Hartree–Fock orbitals are the wrong kind of one-particle building blocks for the molecule. That the extended Koopmans' theorem succeeds in ordering those states of F_2 is an indication that the natural transition orbitals, one-particle functions in a many-body framework, provide a more accurate description of the electron density removed

from neutral F_2 to form the positive ions.

Molecular orbital models based on KT are widely applied in the analysis of photoelectron spectra. Our initial results suggest that EKT, when applied to high quality multiconfiguration wavefunctions, should provide a better one-particle model with which to interpret such experimental data.

Note added in proof: Extended Koopmans' theorem results, χ_k and ϵ_k, for the correlation orbitals ($k = 3\sigma_u$, $2\pi_u$, $2\pi_g$) correspond to so-called "shake-up" states in the photoelectron spectrum of F_2.[5,6] Experimental I. P.'s for the valence shake-up states of molecular fluorine have yet to be reported in the literature. However, judging from analogous values reported for N_2,[21] the F_2 shake-up I. P.'s we have calculated are probably too large.

When performing separate CI calculations on valence shake-up states, other workers have experienced similar difficulties until they added additional diffuse functions to their basis sets.[22] We believe by thus supplementing the basis set of Slater-type orbitals for our neutral wavefunctions, reasonable shake-up I. P.'s can be obtained via the extended Koopmans' theorem.

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[1] T. Koopmans, Physica (The Hague) 1, 104 (1934). Koopmans' theorem asserts that the negative of the Hartree-Fock orbital energies may be taken as variational approximations to a system's (vertical) ionization potentials.

[2] A. C. Wahl, J. Chem. Phys. 41, 2600 (1964).

[3] A. B. Cornford *et al.*, J. Chem. Phys. 54, 2651 (1971).

[4] L. S. Cederbaum, Chem. Phys. Lett. 25, 563 (1974); B. Kellerer, L. S. Cederbaum, and G. Hohlneicher, J. Electron Spectrosc. 3, 107 (1974); L. S. Cederbaum, G. Hohlneicher, and W. von Nissen, Mol. Phys. 26, 1405 (1973).

[5] D. W. Smith and O. W. Day, J. Chem. Phys. 62, 113 (1975); O. W. Day, D. W. Smith, and R. C. Morrison, J. Chem. Phys. 62, 115 (1975); R. C. Morrison, O. W. Day, and D. W. Smith, Int. J. Quantum Chem. Symp. 9, 229 (1975).

[6] M. M. Morell, R. G. Parr, and M. Levy, J. Chem. Phys. 62, 549 (1975).

[7] (a) G. Das and A. C. Wahl, J. Chem. Phys. 56, 3532 (1972); (b) G. Das and A. C. Wahl, Adv. Quantum Chem. 5, 261 (1970); (c) G. Das and A. C. Wahl, J. Chem. Phys. 44, 87 (1966).

[8] J. Hinze, J. Chem. Phys. 59, 6424 (1973), and references therein. Our notation is essentially that of Hinze, except that we use λ instead of ϵ to represent the Lagrange multipliers and our definitions of reduced density matrices γ and Γ are slightly at variance with his.

[9] P. O. Lowdin, Phys. Rev. 97, 1474, 1490, 1509 (1955).

[10] J. C. Slater, Phys. Rev. 91, 528 (1953); R. McWeeny, Proc. R. Soc. (London) Ser. A 232, 114 (1955).

[11] O. W. Day, D. W. Smith, and C. Garrod, Int. J. Quantum

Chem. Symp. **8**, 501 (1974).

[12]P. E. Cade, K. D. Sales, and A. C. Wahl, J. Chem. Phys. **44**, 1973 (1966); P. E. Cade and A. C. Wahl, At. Data Nucl. Data Tables **13**, 339 (1974).

[13]D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, *Molecular Photoelectron Spectroscopy* (Wiley, New York, 1970).

[14]G. Verhaegen, W. G. Richards, and C. M. Moser, J. Chem. Phys. **47**, 2595 (1967).

[15]L. S. Cederbaum, G. Hohlneicher, and W. von Nissen, Chem. Phys. Lett. **18**, 503 (1973).

[16]P. O. Lowdin, Adv. Chem. Phys. **2**, 207 (1959).

[17]G. D. Purvis and Y. Ohrn, J. Chem. Phys. **60**, 4063 (1974).

[18]K. E. Banyard *et al.*, J. Phys. B **7**, 1411 (1974); D. J. Ellis *et al.*, J. Phys. B **6**, L233 (1973).

[19]A. C. Wahl, P. J. Bertoncini, K. Kaiser, and R. H. Land, Argonne National Laboratory Report No. ANL-7271, 1968 (unpublished); G. Das and A. C. Wahl, Argonne National Laboratory Report No. ANL-7955, 1972 (unpublished). It was first necessary for us to repeat the SCF work of Wahl [Ref. 2(a)] and the MC–SCF work of Das and Wahl (Ref. 7). To recalculate the requisite F_2 wavefunctions, we used the BISON and BISON–MC computer programs with which they very generously supplied us, and their previously published basis set parameters. None of the total energies for our recalculated wavefunctions were quite as low as the previously published values, though all were very close, and differences occured only in the sixth significant figure. We attribute the small deficiencies in our versions of the wavefunctions to tolerances for requisite numerical integrations which were slightly larger than those permitted in the original work. To indicate the extent of the small discrepancy, we have shown both Wahl's results [Ref. 2(a)] and our own for the SCF total energies in Table II and the ordinary Koopmans' orbital energies in Table III. The differences in the two sets of Koopmans' orbital energies are nearly negligible. This reinforces our confidence in the extended Koopmans' orbital energies we calculated, since the same computer tape of molecular integrals was used in generating both our SCF and MC–SCF wavefunctions. Compare also Tables VII and VIII of Ref. 7(b) with Tables I and II of this work.

[20]B. T. Pickup, Chem. Phys. Lett. **33**, 422 (1975).

[21]A. W. Potts and T. A. Williams, J. Electron Spectrosc. **3**, 3 (1974).

[22]I. H. Hillier and J. Kendrick, J. Electron Spectrosc. **8**, 239 (1976).