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ABSTRACT

Dyson orbitals, their electron-binding energies, and probability factors provide descriptions of electrons in molecules that are experimentally verifiable and that generalize qualitatively useful concepts of uncorrelated, molecular-orbital theory to the exact limit of Schrödinger's time-independent equation. Dyson orbitals are defined as overlaps between initial, N-electron states and final states with N ± 1 electrons and therefore are useful in the prediction and interpretation of many kinds of spectroscopic and scattering experiments. They also are characteristic of N-electron initial states and may be used to construct electron densities, one-electron properties, and total energies with correlated Aufbau procedures that include probability factors between zero and unity. Relationships with natural orbitals, Kohn–Sham orbitals, and Hartree–Fock orbitals facilitate insights into the descriptive capabilities of Dyson orbitals. Electron-propagator approximations that employ the Dyson quasiparticle equation or super-operator secular equations enable direct determination of Dyson orbitals and obviate the need for many-electron wavefunctions of initial or final states. Numerical comparisons of the amplitudes and probability factors of Dyson orbitals calculated with several self-energy approximations reveal the effects of electron correlation on these uniquely defined, one-electron wavefunctions.

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INTRODUCTION

Orbital terminology continues to influence the formulation and identification of problems in molecular science. Whereas many-electron wavefunctions suffice to determine quantities that are measured in experiments, they are too complicated to invoke a qualitative discussion of all but the simplest molecules or atoms. Such in discourse is an indispensable part of the reasoning by analogy[1] that has propelled the dialectic between chemical-bonding theory and experimentation since the 19th century. Reduction of the information in many-electron wavefunctions being necessary for this purpose, one-electron wavefunctions or energies customarily suffuse discussions that anticipate subsequent experiments or calculations. These terms occupy a central place in the basic curriculum that students attempt to master before undertaking research. They are deeply embedded in the communication of discovery, even as deliberations continue on their ultimate meaning or the possibility of their experimental verification.[2,3] For many scientists, orbital terminology functions chiefly as a mnemonic device for the recall of data or construction of paradigms. Orbitals, pragmatically invoked in these ways, serve an inductive purpose: to facilitate the recognition of patterns in molecular structure, properties, energetics, or reactivity.[4,5]

Orbital concepts have been indispensable in the design and execution of practical, quantum-chemistry algorithms. The motivation of developers is utilitarian: these concepts are introduced only as means to improving standards of accuracy and efficiency. Orbitals underlie construction of many-electron wavefunctions,[6,7] propagators,[8] and density matrices.[9–11] They are an essential instrument in Kohn–Sham theory for the optimization of electron densities.[12] Orthogonalized orbitals make Hamiltonian matrices sparser.[13,14] Canonical, closed-shell, Hartree–Fock orbitals simplify equations of many-body theory.[15] Natural orbitals assist in the recognition of important, correlation effects.[9–11,16] Localized orbitals can economically capture the essence of short-range, electron correlation.[17] Orbital spaces define rules for the selection of configurations in variational calculations.[7] Propitious orderings of orbitals facilitate employment of density-matrix-renormalization-group methods.[18]

TABLE I. Comparison of Hartree–Fock and Dyson-orbital concepts.

Concept	Hartree–Fock picture	Dyson picture
One-electron equation	$(h_1 + J\text{-}K)\phi_p = \varepsilon_p\ \phi_p$	$[h_1 + J\text{-}K + \Sigma(\varepsilon_p)]\phi_p = \varepsilon_p\ \phi_p$
Electron-binding energy	Koopmans ε_p	Correlated ε_p
Probability factor	$P_p = 1$	$P_p = [1 - \delta \langle\phi_p\vert\Sigma(\varepsilon_p)\phi_p\rangle/\delta E]^{-1} \leq 1$
Dyson spin-orbital	ϕ_p	$P_p{}^{1/2}\ \phi_p$
Density matrix, $\rho(x,x')$	$\Sigma_i{}^{\text{occupied}}\ \phi_i(x)\phi_i{}^*(x')$	$\Sigma_p{}^{\text{e detachments}}\ P_p\ \phi_p(x)\phi_p{}^*(x')$
Electronic energy, $\langle H\rangle$	$1/2\Sigma_i{}^{\text{occupied}}\ (h_{1\ ii} + \varepsilon_i)$	$1/2\Sigma_p{}^{\text{e detachments}}\ P_p\ (h_{1\ pp} + \varepsilon_p)$
Electronic density, $\rho(x)$	$\Sigma_i{}^{\text{occupied}}\ \vert\phi_i(x)\vert^2$	$\Sigma_p{}^{\text{e detachments}}\ P_p\vert\phi_p(x)\vert^2$
E^- detachment intensity, T	$\alpha\vert\langle\phi_i\vert T_{op}\ \chi^{\text{continuum}}\rangle\vert^2$	$\alpha\ P_p\vert\langle\phi_p\vert T_{op}\ \chi^{\text{continuum}}\rangle\vert^2$
E^- number sum rule	$N = \Sigma_i{}^{\text{occupied}}\ P_i$	$N = \Sigma_p{}^{\text{e detachments}}\ P_p$

In each of these examples, orbitals are servants of a reductionist project: to deduce molecular properties from the principles of quantum mechanics.

In these inductive and reductive activities, orbitals are regarded as means to an end. They serve merely as aids to pattern recognition or to quantitative prediction. They enable description of physical reality, but they are not part of that reality. Despite the utility of orbital concepts in reasoning by analogy, constants of motion of many-electron Hamiltonians and their wavefunctions are the preferred criteria for assigning spectra.

Can orbitals also be ends? Can the amplitudes and energy of an orbital be verified by an experimental measurement and a corroborating calculation based on reductionist principles? Can orbitals be uniquely defined for all molecular systems without sacrificing their ability to reveal relationships between physical and chemical properties?

Dyson orbitals, their probability factors and associated, electron-binding energies provide affirmative answers to these questions. Dyson-orbital concepts are uniquely defined in terms of many-electron wavefunctions without reference to any mean-field model. Amplitudes of Dyson orbitals are experimentally verifiable. These one-electron wavefunctions are characteristic of transitions between states in which an electron is removed or added, but they also suffice to construct electron densities and one-electron-density matrices of individual states. They provide opportunities to analyze the properties of many-electron systems in terms of one-electron constituents while rigorously accounting for the effects of electron correlation. Exact, correlated total energies can be partitioned into contributions from Dyson orbitals, thus enabling the analysis of molecular shapes and other qualitative features of potential energy surfaces in terms of one-electron energies. Dyson-orbital concepts are completely compatible with standard, probabilistic interpretations of quantum mechanics, Pauli's exclusion principle, and exact descriptions of electron interaction.

Definitions of Dyson spin-orbitals and their probability factors begin this Perspective. The role of Dyson spin-orbitals in the interpretation of transitions between initial and final states for a variety of spectroscopic and scattering experiments follows. Relationships between Dyson spin-orbitals and the properties of initial states are discussed, and examples of the effects of electron correlation on Dyson spin-orbitals are reviewed. Electron-density differences and their connections to Dyson spin-orbitals provide an alternative way to analyze changes in electronic structure that accompany electron detachment or attachment. Comparisons with natural and Kohn–Sham spin-orbitals are made. A direct calculation of Dyson spin-orbitals may be achieved without many-electron wavefunctions through solutions of the Dyson quasiparticle equation of electron-propagator theory, an approach to electronic structure that reveals relationships between total energies, density matrices, and one-electron properties. From this foundation, correlated Aufbau concepts, summarized in Table I, that improve on molecular-orbital doctrines emerge, with rules for the construction of electron densities from Dyson spin-orbitals and their probability factors. The advantages of Dyson and localized spin-orbitals are compared, as are alternative orbital concepts that pertain to initial states and electron binding energies. The mapping of the eigenvalues of the Dyson quasiparticle equation to energies of electron detachment and attachment is reviewed. Residues of the electron propagator are connected to initial-state density matrices. Localization in temporally evolving Dyson orbitals is considered. Perturbative approaches to Dyson spin-orbitals and their electron-binding energies are discussed in terms of the Dyson quasiparticle equation and the equivalent super-operator secular equation. Alternative, many-body approaches that involve the evaluation of many-electron wavefunctions are discussed. Numerical results on molecules and anions display the effects of electron correlation on Dyson spin-orbitals. The section titled Conclusions considers how Dyson-orbital concepts improve on previous, molecular-orbital antecedents and provide a deeper understanding of molecular electronic structure.

DYSON SPIN-ORBITALS AND THEIR PROBABILITY FACTORS

Dyson spin-orbitals of electron detachment and attachment from an initial, N-electron state (Ψ_I) to a final state with N ± 1 electrons (Ψ_F) are defined by the following equations:

$$\varphi_{FI}^{Dyson}(x_1) = \sqrt{N} \int \Psi_F^*(x_2, x_3, x_4, \ldots, x_N) \times \Psi_I(x_1, x_2, x_3, \ldots, x_N)\, dx_2 dx_3 dx_4 \ldots dx_N, \qquad (1)$$

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$$\varphi_{IF}^{Dyson}(x_1) = \sqrt{N+1}\int \Psi_I^*(x_2, x_3, x_4, \ldots, x_{N+1}) \times \Psi_F(x_1, x_2, x_3, \ldots, x_{N+1})dx_2dx_3dx_4\ldots dx_{N+1}, \quad (2)$$

where x_w is the space-spin coordinate of electron w. Integrations over the coordinates of N − 1 or N electrons occur in the two definitions.[8,19] Whereas the usual, overlap integral involves two wavefunctions with the same number of electrons and has a single value, the present integrations yield an overlap *function* between states with different numbers of electrons. The values of the Dyson spin-orbitals at a specific value of x are known as generalized-overlap or Feynman–Dyson amplitudes. (Concepts introduced by the pioneers of quantum electrodynamics have been applied in many fields, including quantum chemistry.[20])

The norms of the Dyson spin-orbitals are called pole strengths, intensity factors, or probability factors (P) and may vary between zero and unity such that

$$0 \le P_{IF} = \int dx \left|\varphi_{IF}^{Dyson}(x)\right|^2 \le 1. \quad (3)$$

Normalized, Dyson spin-orbitals with the usual (i.e., unity) normalization convention, $\phi_{IF}^{Dyson}(x)$, can be written as a product of a Dyson spin-orbital and the inverse, square root of the probability factor,

$$\phi_{IF}^{Dyson}(x) = P_{IF}^{-0.5}\varphi_{IF}^{Dyson}(x). \quad (4)$$

The squared modulus of the overlap integral between Ψ_I and an anti-symmetrized product of a spin-orbital with Ψ_F in Eq. (1) (i.e., for electron detachments) is maximized when that spin-orbital equals the normalized Dyson spin-orbital.[21] A similar relationship is valid for the initial and final states of Eq. (2), which pertains to electron attachments.

Exact probability factors in systems with electron interaction are less than unity for two reasons. First, when spin-orbitals are allowed to relax in calculations on wavefunctions of final states, their overlaps with their counterparts in the initial states are no longer unity, even after they are maximized through a singular-value decomposition[22] (see the discussion of density-difference matrices for Δ-self-consistent-field[23] calculations below). Relaxation effects on Dyson spin-orbitals and their electron-binding energies must be defined in terms of spin-orbital optimization procedures for initial and final states. For a given electron binding energy, at least one of the states must have an odd number of electrons. Therefore, relaxation effects usually are defined in terms of closed-shell,[24,25] unrestricted[26,27] or restricted, open-shell[28] Hartree–Fock *Ansätze*. For transitions that involve one or two states in which there is no dominant Slater determinant, the definition of orbital relaxation can become considerably more complicated.

Second, electron correlation introduces Slater determinants into the initial-state and final-state wavefunctions that may differ by more than one spin-orbital, even when the same set of spin-orbitals is used to construct both wavefunctions. Consider, for example, a closed-shell, Hartree–Fock Slater determinant in the initial state that differs by only one canonical spin-orbital from a frozen-orbital, single-vacancy Slater determinant (i.e., the approximation that follows from Koopmans's identity[29]) in the final state. The same, initial-state Slater determinant differs by three spin-orbitals from a Slater determinant that is singly substituted (i.e., having a promotion from an occupied to a virtual spin-orbital) with respect to the one used to describe the final state in the Koopmans approximation. (Such Slater determinants are called two-hole, one-particle or 2h1p configurations of spin-orbitals and are also known as single shake-up determinants.) The integral in Eq. (1) yields a normalized, canonical, Hartree–Fock spin-orbital in the first case, but the integral vanishes in the second case. Configuration interaction in the initial state can also be responsible for probability factors that are less than unity even when the final state has only a single Slater determinant (*vide infra*).

Because any basis of spin-orbitals can be used to construct full configuration-interaction wavefunctions, it is possible to adopt a terminological convention that considers orbital relaxation to be a kind of correlation effect. This convention will be employed henceforth, and reference to relaxation effects will be minimized unless the analysis of Δ-self-consistent-field[23] calculations is under consideration.

DYSON SPIN-ORBITALS AND TRANSITION INTENSITIES

Sudden transitions[30] between an initial state and an N-electron, final state constructed as an anti-symmetrized product of a state with N − 1 electrons and an orthogonal, continuum spin-orbital, χ, have probabilities, T_{IF}^{sudden}, that are proportional to probability factors and the squared moduli of transition integrals between a normalized, Dyson spin-orbital and χ,

$$T_{IF}^{sudden} \alpha P_{IF}\left|\int \chi^*(x)\hat{T}\phi_{IF}^{Dyson}(x)dx\right|^2. \quad (5)$$

Probability factors therefore provide relative intensities in the sudden approximation when two or more transition integrals may be assumed to be equal, that is,

$$\frac{T_{IF}^{sudden}}{T_{IF'}^{sudden}} = \frac{P_{IF}}{P_{IF'}}. \quad (6)$$

This approximate proportionality has been employed for assignments of principal and shake-up final states in photoelectron spectra and strong-field ionization experiments.[31–33]

Early studies of molecular photoionization intensities adopted a plane-wave approximation to χ.[34–38] The sudden approximation is most valid in photoionization experiments that involve radiation of high energy with respect to electron-binding energies such that the ejected electron's spin-orbital has minimal overlap with spin-orbitals that are at least partially occupied in the initial state.[19,39–42] Under such circumstances, the electric-dipole approximation to the transition operator, $\hat{T}$, may not suffice for the quantitative prediction of transition intensities and therefore contributions from magnetic-dipole, electric-quadrupole, and other terms may be needed.[43] Despite this limitation, calculations that employ only electric-dipole-matrix elements between orthogonalized plane-waves and Dyson orbitals expressed in terms of nuclear-centered, Gaussian functions have proven useful in the interpretation of photoelectron spectra.[32,44–48] Photoionization cross sections that account for

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post-electric-dipole effects have been reported for several molecules in the gas phase.[49] A recent, alternative approach employs the electric-dipole operator and a non-orthogonalized, Coulomb wave in which the latter function's central, nuclear charge becomes an adjustable parameter.[50] In calculations where the initial state is an anion, a plane-wave description of the photoelectron is more appropriate.[51]

Information that pertains to Dyson spin-orbitals may be obtained from electron momentum spectroscopy (EMS), wherein collisions between a gas-phase, target molecule and an electron result in production of two electrons.[52–56] In EMS, momenta of electrons in the target may be inferred from the momenta of the entering electron and the departing pair of electrons. After invoking the plane-wave, impulse approximation, the expression for cross sections reads

$$\sigma_{EMS} \alpha \int d\Omega \, |\, \varphi^{Dyson}(\mathbf{k})|^2, \tag{7}$$

where an average over rotations is performed in the integral. EMS provides experimental data that may be compared directly with calculations of the squared moduli of Dyson spin-orbitals obtained from correlated, *ab initio*, many-electron wavefunctions[57–60] or electron-propagator techniques.[61–66] These calculations have demonstrated the importance of electron correlation in describing the diffuse regions of Dyson spin-orbitals. EMS has been extensively applied to molecules of broad chemical interest, e.g., glycine, and to testing localized and delocalized orbital concepts of chemical bonding.[67–69]

Dyson spin-orbitals in momentum space can be probed by Compton scattering, wherein an incoming photon yields an outgoing photon and an electron.[70,71] After making the reasonable assumption that a plane wave describes the ejected electron, partial-triple-differential-scattering cross sections become proportional to factors of the form shown in Eq. (5). Matrix elements are proportional to Fourier transforms (i.e., the momentum-space representations) of Dyson spin-orbitals. The electron-momentum density is proportional to the total, triple-differential-scattering cross section, which is obtained by summing over its partial counterparts for each final state.

In Penning-ionization, electron spectroscopy,[72] a collision between an excited state of He and a molecule yields a continuum electron and a molecular cation,[73–76]

$$M + \mathrm{He}^* \rightarrow M^+ + \mathrm{He} + e^-. \tag{8}$$

The helium atom is a convenient choice, for its excitation energy exceeds the valence-ionization energies of typical molecules. Cross sections obtained with a given kinetic energy of the ejected electron are proportional to the squared moduli of exchange-electron-repulsion integrals that involve a Dyson spin-orbital, a continuum function, and the 2s and 1s orbitals of the helium atom. These data constitute a sensitive probe of the diffuse regions of Dyson spin-orbitals.

An interpretation of angle-resolved, photoelectron spectra[77] (ARPES) that assumes the sudden approximation for final states, the uniformity of the electromagnetic vector-potential ($\mathbf{A}$), neglect of Auger effects, and a plane-wave ($e^{i\mathbf{k}^*\mathbf{r}}$) description of the emitted electron yields a simple relationship between transition probabilities (W_{IF}) and Fourier transforms of Dyson spin-orbitals.[78,79] This proportionality may be expressed as

$$W_{IF} \alpha |\mathbf{A} \cdot \mathbf{k}|^2 \left|\varphi^{Dyson}(\mathbf{k})\right|^2. \tag{9}$$

Provided that the four assumptions are valid, ARPES intensities correspond to cuts of the modulus of the momentum representation of a Dyson spin-orbital, with the radius of the cut depending on the momentum vector of the photoelectron. Experiments on molecules oriented by absorption on surfaces have been able to identify various kinds of σ and π orbitals by comparing the observed and predicted maps of intensities.[80]

Interpretations of ionization spectroscopy that are founded on the squared moduli of Dyson spin-orbitals may safely ignore any loss of phase information. This deficiency in the characterization of Dyson spin-orbitals can be overcome in some cases by taking account of the size or symmetry of a molecular target with polarized light.[81] After making some reasonable assumptions on the spatial extents of the Dyson spin-orbitals, it is possible to construct iterative algorithms that yield phase information.[82] A general approach, known as orbital tomography, employs phase-retrieval algorithms used in coherent-diffraction imaging and has been applied to molecules oriented by absorption on surfaces.[83–85] Dyson spin-orbitals that pertain to the lowest, ionization energies of weakly bound, organic molecules absorbed on metallic surfaces have been characterized, and phase patterns that result in bonding or antibonding relationships between nuclei have been inferred.

Tomographic imaging of Dyson spin-orbitals can be realized via field ionization of aligned molecules in the gas phase followed by re-collision of the emitted electron with the target induced by laser fields.[86] The resulting, oscillating dipoles emit high-harmonic radiation whose amplitude, phase, and polarization may be measured. A Fourier transform of the product of the dipole operator and the Dyson spin-orbital of the lowest, ionization energy is thereby determined.

The variety of techniques and the abundance of chemical applications that are described by Dyson spin-orbitals are evidence of the relevance of this concept in understanding molecular electronic structure. In each class of experiments, information on transitions from a selected initial state to a variety of final states can, in principle, be aggregated to characterize an initial state's properties.

DYSON SPIN-ORBITALS, ELECTRON DENSITIES, AND PROPERTIES

In addition to describing bound-continuum, transition intensities, Dyson spin-orbitals also provide information about initial-state properties, such as the electron density. The one-electron, reduced-density matrix of an initial, N-electron state,[9]

$$\gamma_I(x, x') = N \int dx_2 dx_3 dx_4 \ldots dx_N \Psi_I(x, x_2, x_3, \ldots, x_N) \times \Psi_I^*(x', x_2, x_3, \ldots, x_N), \tag{10}$$

after insertion of a complete set of final states with N − 1 electrons and employment of Eqs. (1) and (4) reads

$$\gamma_I(x,x') = \sum_F{}' \varphi_F^{Dyson}(x)\left[\varphi_F^{Dyson}(x')\right]^* = \sum_F{}' P_F \phi_F^{Dyson}(x)\left[\phi_F^{Dyson}(x')\right]^*. \quad (11)$$

(The initial-state indices of the Dyson spin-orbitals, normalized, Dyson spin-orbitals, and probability factors have been omitted for brevity; note that the primed summation includes final states with N − 1 electrons and no final states with N + 1 electrons.) The expectation value of a one-electron operator, O_1, may be resolved into its normalized Dyson spin-orbital components such that

$$\langle O_1 \rangle = \sum_F{}' P_F \left\langle \phi_F^{Dyson} \middle| O_1 \phi_F^{Dyson} \right\rangle. \quad (12)$$

The initial state's electron density at space-spin coordinate x, $\rho_I(x)$, likewise consists of Dyson spin-orbital contributions in the expression

$$\rho_I(x) = \gamma_I(x,x) = \sum_F{}' P_F \left|\phi_F^{Dyson}(x)\right|^2. \quad (13)$$

Probability factors simultaneously convey information about transitions and initial states after integrating over all space and spin coordinates to obtain the sum rule,

$$\int dx \rho_I(x) = N = \sum_F{}' P_F. \quad (14)$$

In general, the summations over F may comprise principal, final states with probability factors near unity (e.g., cases where Koopmans's identity[29] is qualitatively valid) and copious correlation final states (e.g., shake-ups) with low probability factors. The Dyson spin-orbitals constitute an over-complete, non-orthogonal set of one-electron functions. Each term in the summation over F is physically meaningful and has potential utility in interpretations of chemical bonding that assume knowledge of γ or ρ. (Examples include the quantum theory of atoms in molecules[87] and natural-bond-order theory.[88]) Many qualitative indices of electronic structure, including atomic charges and bond orders, may be decomposed into Dyson-spin-orbital components. Relationships between frontier-molecular orbitals and patterns of chemical reactivity[1,4,5,89,90] (such as electrophilicity and nucleophilicity) may be generalized from their original, uncorrelated context by employing Dyson spin-orbitals that incorporate the effects of electron correlation and that are subject to experimental examination. Dyson spin-orbitals of atoms and molecules decay asymptotically (i.e., as $R \rightarrow \infty$) according to the function $R^B e^{-\sqrt{2\omega}R}$, where ω is the corresponding ionization energy and $B = (2\omega)^{-\frac{1}{2}} - 1$.[91,92]

For an uncorrelated initial state, one may, in accord with Pauli's requirement of anti-symmetrized wavefunctions for many-electron systems, assign N electrons to N spin-orbitals in the N! ways that are characteristic of a Slater determinant. In this limit, there is no ambiguity in the role of the occupied spin-orbitals in assembling the electron density: the probability that an electron is assigned to one of these spin-orbitals is unity. The spin-orbital contributions to one-electron properties, such as kinetic energy, are equally definite.

Once electron-interaction terms appear in the Hamiltonian, such certainty is abolished. One cannot describe one-electron properties that depend on off-diagonal elements of the one-electron, reduced-density matrix (e.g., kinetic energy) of an N-electron system with only N spin-orbitals. (For properties that depend only on the diagonal elements of the one-electron, reduced-density matrix, the electron density suffices.) The electron density and the one-electron, reduced-density matrix now have contributions from the much larger set of Dyson spin-orbitals that correspond to final states with N − 1 electrons. The squared modulus of a given Dyson spin-orbital contributes a quantity of electron density equal to its probability factor; the sum of these contributions equals N. These factors may be understood as summable, transition probabilities associated with their corresponding, Dyson spin-orbitals. If all the matrix elements of $\hat{T}$ in Eq. (5) were equal, transition intensities that pertain to final states with N − 1 electrons would be proportional to these probabilities. The predicted photoelectron spectrum would provide a definite, albeit probabilistic, mapping between intensities and spin-orbitals.

WEAK AND STRONG CORRELATION

The weak-correlation limit for a many-electron system occurs when one-electron terms in a Hamiltonian dominate the two-electron terms. In such cases, the N-electron, initial state approaches a single, Slater determinant built with spin-orbital eigenfunctions of the one-electron Hamiltonian. Final states with N ± 1 electrons become Slater determinants that differ from that of the initial state only by annihilating an electron in a hitherto occupied spin-orbital or by adding an electron to a hitherto unoccupied spin-orbital. Dyson spin-orbitals equal these eigenfunctions and their probability factors equal unity. There are only N non-vanishing terms in Eq. (13). Transitions to other, final states with more than one change in spin-orbital occupation number with respect to the initial determinant have vanishing probability factors.

The Fock operator generated in a stable, closed-shell, Hartree–Fock calculation provides an example of a model Hamiltonian without correlation. The absence of correlation yields Dyson spin-orbitals that are equal to canonical Hartree–Fock spin-orbitals. For this model Hamiltonian, there are only N non-vanishing terms in Eqs. (11)–(14).

For typical, closed-shell molecules, perturbative corrections associated with the introduction of the Møller–Plesset fluctuation potential[93] produce Dyson spin-orbitals for the lowest ionization energies and largest electron affinities that strongly resemble canonical, Hartree–Fock spin-orbitals, but with probability factors near 0.9.[94–97] The deviation of the probability factor from unity is a consequence of electron correlation. In some cases, such consequences can be confined to the initial or final state. In H_2, for example, expansion of the full-configuration-interaction wavefunction in terms of the exact spin-orbitals of H_2^+ produces a dominant determinant with a doubly occupied $1\sigma_g$ orbital. The Dyson spin-orbital is composed chiefly of the same $1\sigma_g$ spin-orbital with minor, interfering contributions from higher, $n\sigma_g$ ($n > 1$) spin-orbitals of H_2^+ that originate from single replacements (i.e., $1\sigma_g n\sigma_g$ configurations) with respect to the dominant determinant. The probability factor is less than unity because of the presence of determinants without the $1\sigma_g$ orbital in the H_2 wavefunction. Even in the absence of electron correlation in one of the states, probability factors can deviate from unity.

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Copious, correlation states with low probability factors appear at higher energies, and their Dyson spin-orbitals may have contributions from more than one canonical, Hartree–Fock spin-orbital.[31] This trend underlies the manifest breakdown of the uncorrelated, molecular-orbital picture mentioned above in the inner-valence-energy region of photoelectron spectra and has been extensively documented by experiment and calculation.[31] Quasi-degeneracy between occupied, inner-valence, spin-orbital energies and the sum of two, occupied, outer-valence, spin-orbital energies minus a low-lying, virtual, spin-orbital energy (i.e., a zeroth-order, shake-up energy) typically foreshadows the appearance of numerous correlation states that have no clear counterpart at the uncorrelated, frozen-orbital (i.e., Ref. 29) level of theory. In such cases, correlation effects are much stronger in final states than in initial states and the Koopmans picture is obliterated. Despite this complication, every final state has its Dyson spin-orbital and probability factor. Schemes for efficiently performing summations over these final states to produce densities or properties are discussed below.

For strongly correlated, initial states, even electron-binding energies with the smallest, absolute values may be accompanied by probability factors that are far from unity. For example, the ^{1}S state of the carbon atom in a 2p complete-active-orbital space (with 1s and 2s orbitals in an inactive core) has the following, multi-configurational wavefunction:

$$\Psi = 3^{-0.5}\left(||\cdots\psi_{1\alpha}\psi_{-1\beta}|| + ||\cdots\psi_{-1\alpha}\psi_{1\beta}|| - ||\cdots\psi_{0\alpha}\psi_{0\beta}||\right), \qquad (15)$$

where the active, atomic spin-orbitals in the three Slater determinants have m_l and m_s subscripts. A single, Slater determinant suffices to describe each of the six, degenerate, ^{2}P states of the carbon cation. For a frozen, active-orbital space, each of the six, normalized, Dyson spin-orbitals equals one of the atomic spin-orbitals, each of the probability factors equals one third and the sum of probability factors equals the number of active electrons, two. Even in the absence of electron correlation in the final states, probability factors can be much lower than unity. Electron correlation in initial states also can underlie the appearance of correlation final states that are dominated by two-hole–one-particle configurations of spin-orbitals with respect to an initial state's reference determinant. For the ^{1}S state of the beryllium atom in a 2s-2p, complete-active space, the wavefunction reads

$$\Psi = \lambda||\cdots\psi_{s\alpha}\psi_{s\beta}|| + \left(\frac{1-|\lambda|^2}{3}\right)^{0.5} \times \left(||\cdots\psi_{1\alpha}\psi_{-1\beta}|| + ||\cdots\psi_{-1\alpha}\psi_{1\beta}|| - ||\cdots\psi_{0\alpha}\psi_{0\beta}||\right). \qquad (16)$$

The sums of probability factors for the ^{2}S and ^{2}P final states are $2|\lambda|^2$ and $2(1-|\lambda|^2)$, respectively. The ^{2}P states are shake-ups with respect to the closed-shell, $2s^2$, reference configuration and the corresponding Dyson spin-orbitals are 2p functions. Intensity ratios therefore have the potential to reveal the strength of electron correlation (i.e., the deviation of $|\lambda|$ from unity) in the reference state.

DYSON SPIN-ORBITALS AND ELECTRON-DENSITY DIFFERENCES

The squared modulus of a Dyson spin-orbital equals the electron-density difference between initial and final states only in the uncorrelated limit.[98] Therefore, Fukui functions[99] (postulated, electron-density derivatives typically approximated by differences between N-electron and N ± 1-electron ground states) and electron densities (i.e., squared moduli) associated with Dyson spin-orbitals are equivalent at the frozen-orbital, Hartree–Fock level of theory. Higher levels of theory yield Dyson spin-orbitals whose norms are less than unity. In perturbative approaches that employ the Møller–Plesset fluctuation potential,[93] the largest term in the electron-density difference for a Koopmans-like final state is the squared modulus of the Dyson spin-orbital.[100–102] Probability factors, being the integrated, squared moduli of the Dyson spin-orbitals, therefore are indices of the importance of electron correlation in describing final states.

Because the squared modulus of a Dyson spin-orbital is always non-negative, it cannot describe accumulation of electron density when final states have $N-1$ electrons or depletion of electron density when final states have $N+1$ electrons. (Such results imply Fukui functions with negative values.[103]) To describe such effects, it is necessary to procure differences of electron densities between initial and final states. When the difference of one-electron reduced density matrices between initial (N electron) and final (N ± 1 electron) states is diagonalized, the absolute value of the sum of the eigenvalues equals unity, but the individual eigenvalues may be positive or negative. For a closed-shell molecule where Koopmans's identity is qualitatively valid (with the Dyson spin-orbital being well approximated by a canonical, Hartree–Fock spin-orbital), there will be an eigenfunction of the density-difference matrix (with an eigenvalue close to unity) that closely resembles the Dyson spin-orbital. For a simple shake-up final state with a low probability factor in which even a single, configuration-state function (i.e., a symmetry-adapted combination of Slater determinants) with three open shells dominates, there may be little resemblance between the squared modulus of the normalized Dyson spin-orbital and the difference of electron densities.

Natural-ionization spin-orbitals are eigenfunctions of the difference of initial-state and final-state reduced density matrices with N and $N-1$ electrons, respectively. A density-difference matrix produced with single-determinantal wavefunctions for the initial and final states has a single, unit eigenvalue and $N-1$ pairs of eigenvalues, $(z, -z)$, that sum to zero, where $0 \le z \le 1$.[22] For low-lying final states in which a Koopmans picture is qualitatively reasonable (i.e., where all values of z are close to zero and far from unity), the squared modulus of the spin-orbital with the unit eigenvalue provides the principal component of the change in the electron density. The spin-orbitals with the paired eigenvalues provide insights into the adaptation of the remaining $N-1$ electrons to the removal of an electron from the spin-orbitals with the unit eigenvalue. This analysis of orbital relaxation effects is applicable to Δ-SCF (self-consistent-field) calculations[23] or to any cases in which the initial and final states have idempotent, reduced-density matrices. For the initial and final states of Koopmans's identity, all $N-1$ values of z vanish, for an absence of relaxation in the final-state spin-orbitals is postulated. Kohn–Sham determinants, whose chief purpose is to produce an electron-density function with Fermionic characteristics, have nonetheless supplied idempotent, reduced-density matrices of initial and final states for this analysis in several applications.[104,105]

The effects of orbital relaxation from initial-state to final-state determinantal wavefunctions may be clarified by performing a

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singular-value decomposition on the rectangular matrix whose elements are overlaps between the two sets of occupied spin-orbitals.[106] The resulting corresponding spin-orbitals[107] do not change the two determinantal wavefunctions (except perhaps by a phase factor) and have a diagonal overlap matrix. (The diagonal elements may have absolute values from zero to unity.) One of the spin-orbitals is orthogonal to all the others, and its squared modulus represents the principal change in the electron density. The remaining N − 1 pairs of initial and final spin-orbitals have maximized overlaps, S, which are related to their corresponding value of z by $z^2 = (1 - |S|^2)$.[22] After removal of an electron from the former, principal spin-orbital in the initial-state determinant, maximum overlaps between the initial state's and the final-state's spin-orbitals are in effect. The principal, natural-ionization spin-orbital equals the normalized Dyson spin-orbital; the probability factor equals the product of the squares of the N − 1 paired-spin-orbital overlaps. Shake-up final states will display one or more values of z that can approach unity.

Natural-ionization spin-orbitals may be extracted from any density-difference matrix, but those that arise from correlated calculations do not necessarily produce the paired eigenvalues obtained with single-determinant wavefunctions. Positive and negative eigenvalues correspond to natural-ionization spin-orbitals that, respectively, describe electron depletion and accumulation in the final state with respect to the initial state. In electron-propagator calculations, density-difference matrices have been employed in the evaluation of final-state, one-electron properties, including gradients with respect to nuclear positions. For example, in second-order-self-energy calculations, the elements of the density-difference matrix in the canonical Hartree–Fock basis may be evaluated with algorithms that have quartic arithmetic scaling.[100–102] In non-Dyson, electron-propagator methods,[108] final-state wavefunctions give rise to density-difference matrices that also are easily evaluated.

DYSON SPIN-ORBITALS AND NATURAL SPIN-ORBITALS

Natural spin-orbitals, ϕ^{nat}, are eigenfunctions of the one-electron, reduced-density matrix whose eigenvalues or occupation numbers, n_p^{nat}, sum to N.[9–11] The number of natural orbitals produced in a calculation is determined by the dimension of the spin-orbital basis, M. The Hermiticity of the one-electron, reduced-density matrix derived from variational calculations guarantees the orthonormality of the natural spin-orbitals. The eigenvalues, which may have values between zero and unity, provide a prioritized list of spin-orbitals for inclusion in a variational calculation that optimizes overlap with a reference wavefunction. (In some classes of non-variational calculations, the positivity of the eigenvalues is not guaranteed.) The one-electron, reduced-density matrix of an N-electron initial state may be expressed in terms of M orthonormal, natural spin-orbitals or Dyson spin-orbitals that correspond to observable transitions,

$$\begin{aligned}\gamma_I(x,x') &= \sum_{p=1}^{M} n_p^{nat}\phi_p^{nat}(x)\left[\phi_p^{nat}(x')\right]^* \\ &= \sum_F{}' P_F\phi_F^{Dyson}(x)\left[\phi_F^{Dyson}(x')\right]^* \\ &= \sum_F{}' \varphi_F^{Dyson}(x)\left[\varphi_F^{Dyson}(x')\right]^*. \end{aligned} \tag{17}$$

In variational calculations, the sum rule $\sum_{p=1}^{M} n_p^{nat} = N$ is always obeyed, regardless of the quality of the wavefunction. As basis sets and wavefunction flexibility approach the exact limit, additional natural spin-orbitals with eigenvalues close to zero appear, with minimal changes to the terms with the highest natural occupation numbers. (This theme has been amply explored and exploited in the context of basis-set optimization.[109,110]) Equation (14) provides an alternative criterion for judging the quality of a one-electron, reduced-density matrix whose Dyson-spin-orbital components are subject to experimental confirmation or refutation.

Canonical orthogonalization of the Dyson spin-orbitals of electron detachment expressed in terms of M independent functions yields only M natural spin-orbitals.[98] In general, these Dyson spin-orbitals are linearly dependent, for the number of final states with N − 1 electrons far exceeds M. Only in the absence of electron interaction do the Dyson spin-orbitals with non-zero probability factors form an orthonormal set. After defining the overlap matrix of the Dyson spin-orbitals with

$$\Delta_{FF'} = \left\langle \varphi_F^{Dyson} \middle| \varphi_{F'}^{Dyson} \right\rangle, \tag{18}$$

its M non-zero eigenvalues and their eigenvectors are given by

$$\mathbf{\Delta U} = \mathbf{U}\mu. \tag{19}$$

(Matrices are represented by bold type.) The natural-spin-orbital, occupation numbers are the non-zero eigenvalues of the overlap matrix of the Dyson spin-orbitals of electron detachment, i.e., $n_p^{nat} = \mu_p$. The natural spin-orbitals may be expressed as

$$\phi_p^{nat} = \sum_F{}' \varphi_F^{Dyson} U_{Fp}\mu_p^{-0.5}, \tag{20}$$

where the summation again occurs only over final states with N − 1 electrons. Natural occupation numbers are related to overlaps between natural and Dyson spin-orbitals through

$$\begin{aligned} n_p^{nat}\delta_{pq} &= \sum_F{}' \left\langle \phi_p^{nat} \middle| \varphi_F^{Dyson} \right\rangle \left\langle \varphi_F^{Dyson} \middle| \phi_q^{nat} \right\rangle \\ &= \sum_F{}' P_F \left\langle \phi_p^{nat} \middle| \phi_F^{Dyson} \right\rangle \left\langle \phi_F^{Dyson} \middle| \phi_q^{nat} \right\rangle. \end{aligned} \tag{21}$$

Equations (20) and (21) establish that natural spin-orbitals and their occupation numbers may be decomposed into more fundamental and experimentally accessible, Dyson-spin-orbital constituents.

Occupation numbers (i.e., normalized-orbital expectation values of the density operator) that occur in population analyses of individual states may be calculated for normalized Dyson spin-orbitals. Each of these occupation numbers exceeds its corresponding probability factor and their sum exceeds N. Despite ambiguities associated with overlapping or overcomplete sets of orbitals, connections between experimental measurements and occupation numbers defined in various ways can have qualitative utility.

APPROXIMATE DYSON SPIN-ORBITALS FROM KOHN–SHAM DETERMINANTS

The one-electron operator that appears in the Kohn–Sham equations[12] may differ from the Fock operator of the Hartree–Fock

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equations in its treatment of exchange and correlation, and its original purpose was to generate a Slater determinant and a corresponding electron density. Eigenfunctions of the Kohn–Sham operator can be excellent approximations to Dyson spin-orbitals of closed-shell molecules with probability factors close to unity.[111] Density functionals have been reparameterized to yield spin-orbital energies that are within a few tenths of an eV of experiment for representative sets of molecules.[112–115] The model, one-electron Hamiltonian of Kohn–Sham theory may be adjusted to overcome deficiencies in approximate self-energies such as those used in the GW family of methods.[116] This operator provides a convenient and accurate successor to empirical, tight-binding Hamiltonians that efficiently generate molecular orbitals for the analysis of chemical bonding.[117] The chief deficiencies of this approach to procuring Dyson spin-orbitals are those that pertain to any one-electron Hamiltonian: all non-vanishing, probability factors equal unity and there are no accessible correlation (shake-up) states. Inner-valence, spin-orbital energies obtained in this way represent at best an average over many final states.

OBTAINING DYSON SPIN-ORBITALS FROM CORRELATED, ONE-ELECTRON OPERATORS

Dyson spin-orbitals are eigenfunctions of an energy-dependent (i.e., E-dependent), non-local, one-electron operator in the Dyson quasiparticle equation,[95,118–125]

$$[f + \Sigma(E)]\phi_F^{Dyson} = \phi_F^{Dyson}\epsilon_F. \tag{22}$$

The Fock (f) term in the operator has Coulomb and exchange components that depend on the one-electron, reduced-density matrix of the initial state. The energy-dependent, self-energy operator, $\Sigma(E)$, depends on the initial state's second- and higher-order reduced-density matrices. Diagrammatic and algebraic approaches to deriving approximate versions of the self-energy matrix are subject to systematic improvements that approach the exact limit.[8,126,127] The solution of the eigenvalue equation supplies the normalized Dyson spin-orbital but does not suffice to determine probability factors. Energy derivatives of $\mathbf{\Sigma}(E)$ matrix elements provide the missing information in

$$P_F = \left(1 - \frac{d\left\langle\phi_F^{Dyson}\middle|\Sigma(E)\phi_F^{Dyson}\right\rangle}{dE}\right)^{-1}. \tag{23}$$

In practice, $\mathbf{\Sigma}(E)$ may be calculated at several values of the energy until the latter variable becomes equal to an eigenvalue, ϵ_F. When self-consistency is attained in Eq. (22) (i.e., when $E = \epsilon_F$), the derivative in Eq. (23) is evaluated to give the probability factor, P_F, and therefore the Dyson spin-orbital, φ_F^{Dyson}.

Each of the self-consistent eigenvalues ϵ_F equals an electron-binding energy. As more terms are added to the self-energy operator and as basis sets are improved, exact results may be approached. This conclusion is applicable to all varieties of final states, regardless of probability factors. Because of the energy dependence of the $\Sigma(E)$ operator, the number of solutions (corresponding to poles and residues of the electron propagator) far exceeds M, the dimension of the spin-orbital basis.

As the f operator depends on the one-electron, reduced-density matrix of the initial state, corrections to canonical, Hartree–Fock spin-orbital energies may be present in its matrix elements. These terms are sometimes denominated constant self-energy contributions. Because they do not vanish as the absolute value of E increases without bound, they are often denoted by $\Sigma(\infty)$. [Matrix elements of $\Sigma(E)$ approach zero as $|E| \to \infty$.] In many cases where Kohn–Sham spin-orbitals and their energies are employed, energy-independent terms that arise from the difference between the exchange operator and the exchange–correlation potential also are incorporated into the self-energy corrections to the Kohn–Sham, spin-orbital energies.

DYSON SPIN-ORBITALS AND TOTAL ENERGIES

The total electronic energies that underlie potential energy hypersurfaces may be resolved into contributions from Dyson spin-orbitals according to

$$\langle H\rangle = \frac{1}{2}\sum_F{}' P_F(\langle\phi_F^{Dyson}|h_1\phi_F^{Dyson}\rangle + \epsilon_F), \tag{24}$$

where h_1 is the one-electron (kinetic plus nuclear-attraction) component of the Hamiltonian operator, H.[8,95,120] By replacing the Fock operator with its one-electron, Coulomb (J) and exchange (K) constituents and employing the Dyson quasiparticle equation (22), one may separate the electron-interaction terms, which have coefficients of one half, in the expression

$$\langle H\rangle = \sum_F{}' P_F\langle\phi_F^{Dyson}|\left(h_1 + \frac{1}{2}[J - K + \Sigma(E)]\right)\phi_F^{Dyson}\rangle. \tag{25}$$

The total energy of an initial state consists of measurable quantities (i.e., the Dyson spin-orbitals and their electron-binding energies) such that

$$\langle H\rangle = \frac{1}{2}\sum_F{}'\langle\varphi_F^{Dyson}|(h_1 + \epsilon_F)\varphi_F^{Dyson}\rangle. \tag{26}$$

Equations (22) and (23) therefore are the conceptual foundation of relationships between electron detachment energies and initial-state properties such as total energies, electron densities, dipole moments, momentum distributions, and so forth. Dyson spin-orbitals that connect initial, N-electron states to final states with N − 1 electrons are the fundamental units that occur in each summation. Equation (26) generalizes total energy expressions based on summations over occupied spin-orbitals (obtained with Hartree–Fock calculations or by other means), which have been employed to explain trends in molecular shapes with Walsh diagrams.[128–130]

In the uncorrelated, closed-shell or unrestricted Hartree–Fock approximations, there are only N non-vanishing pole strengths (each of which equals unity), the Dyson spin-orbitals equal their canonical, Hartree–Fock counterparts and the electron-detachment energies are those given by Koopmans's identity. Hartree–Fock, total energies therefore are expressed in terms of canonical spin-orbitals (CSOs) as

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$$\langle H\rangle = \frac{1}{2}\sum_{i}^{occupied}\left(\langle\phi_i^{CSO}|h_1\phi_i^{CSO}\rangle + \epsilon_i^{Koopmans}\right), \tag{27}$$

but, because of the invariance of Slater determinants with respect to unitary transformations of their spin-orbitals,[131] these total energies can also be assembled in terms of localized spin-orbitals (LSOs), where

$$\langle H\rangle = \frac{1}{2}\sum_{i}^{occupied}\left(\langle\phi_i^{LSO}|h_1\phi_i^{LSO}\rangle + \langle\phi_i^{LSO}|f\phi_i^{LSO}\rangle\right). \tag{28}$$

The latter terms, having no connection to energies of electron detachment or to Dyson spin-orbitals and lacking a unique localization procedure for their generation, obliterate relationships between properties of stationary initial and final states.

To encompass the effects of electron correlation on total energies, more than N spin-orbitals must be recruited. The Dyson quasiparticle equation can be employed to accomplish this aim by generating final states with N − 1 electrons that are much more numerous than the number of electrons. Explicit consideration of all the final states required to recover the summations of Eqs. (24)–(26) may be avoided with contour integrations in the complex plane.

INITIAL-STATE PROPERTIES FROM THE ELECTRON PROPAGATOR

The electron propagator matrix, $\mathbf{G}(E)$, may be related to the Fock and energy-dependent, self-energy matrices via

$$\mathbf{G}(E) = [E\mathbf{1} - \mathbf{f} - \mathbf{\Sigma}(E)]^{-1}. \tag{29}$$

Total energies may be expressed as

$$\langle H\rangle = Trace\left[\frac{1}{4\pi i}\oint_c(\mathbf{h}_1 + E\mathbf{1})\mathbf{G}(E)dE\right], \tag{30}$$

where the c subscript denotes a contour in the complex plane that encloses all electron-detachment energies and no attachment energies.[8] Evaluation of the electron propagator matrix at a small number of complex values of E that are not close to electron-detachment energies (which are real numbers) is usually more efficient than obtaining contributions to the total energy from each Dyson spin-orbital of electron detachment. Most of these numerous contributions have small probability factors and pertain to high energies of electron detachment. Their collective contributions are easier to evaluate by employing the contour integral of Eq. (30).

A simpler contour integral yields the spin-orbital-density matrix,

$$\boldsymbol{\gamma} = \frac{1}{2\pi i}\oint_c\mathbf{G}(E)dE. \tag{31}$$

The collective contributions of the Dyson spin-orbitals to one-electron properties (such as the dipole moment) therefore may be evaluated efficiently with

$$\langle O_1\rangle = Trace(\mathbf{O}_1\boldsymbol{\gamma}). \tag{32}$$

DYSON SPIN-ORBITALS AND RESIDUES OF THE ELECTRON PROPAGATOR

The electron-propagator matrix[8,132,133] may be expressed in terms of Dyson spin-orbitals and electron binding energies as follows: Let Dyson spin-orbitals be expanded in terms of M orthonormal functions, χ, according to

$$\phi_F^{Dyson} = \sum_{p=1}^{M}\chi_p C_{pF}. \tag{33}$$

In its spectral, energy-dependent representation, the electron-propagator matrix reads

$$G_{rs}(E) = \lim_{\eta\to +0}\left(\sum_{F}^{N+1e^-}\frac{C_{rF}C_{sF}^*}{E-\epsilon_F+i\eta} + \sum_{F}^{N-1e^-}\frac{C_{rF}C_{sF}^*}{E-\epsilon_F-i\eta}\right). \tag{34}$$

The two summations refer to attachments or detachments of electrons to yield final states with N ± 1 electrons. The values of E that cause matrix elements to increase without bound (i.e., approach infinity) are known as poles and correspond to electron-binding energies. The numerator of such a singular term is called a residue and provides the r–s contribution to the squared modulus of the corresponding Dyson spin-orbital. Note that the energy parameter, in general, is defined to be a complex number. For a given pole, a sum over residues of diagonal matrix elements suffices to produce a pole strength (probability factor),

$$P_F = \sum_{r=1}^{M}|C_{rF}|^2. \tag{35}$$

The indices r and s may refer to any set of orthonormal spin-orbitals. For example, symmetrically orthogonalized, atomic, natural spin-orbitals[134] could be employed to yield atomic, bond, hybridized or other kinds of contributions to a given Dyson spin-orbital.

The spin-orbital-density matrix, $\mathbf{\Pi}$, of uncorrelated, molecular-orbital theory matrix may be generalized with

$$\Pi_{rs} = \sum_{F}{}' C_{rF}C_{sF}^* \tag{36}$$

so that

$$\gamma_I(x,x') = \sum_{r,s=1}^{M}\chi_r(x)\Pi_{rs}\chi_s^*(x'). \tag{37}$$

The summation of Eq. (36) may be avoided by evaluating the contour integral of Eq. (31) for $G_{sr}(E)$.

CORRELATED AUFBAU PRINCIPLES

Natural spin-orbitals are generally conceded to be characteristic of a given state. Equation (17) establishes that Dyson-spin orbitals are equally characteristic of N-electron initial states and that they have the additional advantage of mapping uniquely (i.e., one-to-one) onto final states with N − 1 electrons. Transitions observed between initial and final states provide experimental tests (via, for example, EMS or ARPES) for the verification of Dyson spin-orbitals calculated with Eqs. (22) and (23) or by less direct means that require

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the evaluation of many-electron wavefunctions and integration of their products according to Eq. (1) or (2). The Dyson spin-orbital concept requires no introduction of model Hamiltonians, especially those that are free of electron interaction, or approximations of many-electron states by lone Slater determinants or other limited, configuration-interaction *Ansätze*.

Resolving the interpretive dilemma of state-specific vs transition orbitals requires a modification of several, traditional, molecular-orbital concepts (such as probability factors of unity or the assumption that density differences equal squared moduli of Dyson orbitals[135,136]) in which electron correlation has been ignored.

1. In the presence of electron interaction, the squared modulus of a Dyson spin-orbital is not equal to the electron-density difference between an initial, N-electron state and a final state with N − 1 electrons,

$$\Delta\rho(x) = \rho_I(x) - \rho_F(x) \neq |\varphi_{FI}^{Dyson}(x)|^2. \tag{38}$$

   Only in the absence of electron interaction can equality be restored.
2. For correlated systems, Dyson spin-orbitals are not normalized to unity. Equality with unity in Eq. (3) is realized only in the absence of electron correlation; otherwise, probability factors lie between unity and zero. When electron interaction is neglected, there are N final states with N − 1 electrons that have probability factors of unity, and therefore, the associated probability that an electron has been ejected from an occupied spin-orbital is equal to one. In the final state of this approximation, the formerly occupied spin-orbital now is completely unoccupied. In an interacting system (one in which electron correlation is present), the probability factor associated with a given Dyson spin-orbital is less than one. The sum of these probabilities [see Eq. (14)] equals the number of electrons in the initial state, N. In the final state, the normalized Dyson spin-orbital may be partially occupied (i.e., have a non-zero expectation value of the electron-density operator) because of electron correlation. Probability factors are indices of the importance of electron correlation and final-state relaxation of spin-orbitals for a given transition.
3. The number of non-vanishing, Dyson spin-orbitals that correspond to final states with N − 1 electrons is much larger than N for systems with electron interaction. This result has been abundantly confirmed by photoelectron experiments. In the familiar terminology of configuration interaction, most of the numerous, closely spaced peaks of the inner-valence (high-electron-binding energy) spectral region have been assigned to final, many-electron wavefunctions wherein configurations with three or more spin-orbital differences with respect to a reference Slater determinant (e.g., two vacancies in the occupied spin-orbitals and one added electron in the virtual spin-orbitals of the reference determinant) dominate and where the frozen-orbital, single-vacancy Slater determinants (e.g., those of Koopmans's identity) are unimportant. Dyson spin-orbitals offer a succinct characterization of the broad spectral features that arise from many transitions, each with a low probability factor. The inevitable appearance of such inner-valence spectra in molecules is evidence of electron correlation, for an uncorrelated model would predict non-vanishing intensity only for N final states described by single-vacancy determinants. For correlated systems, it is incorrect to state that a transition of electron detachment annihilates an electron in a normalized Dyson spin-orbital, for this function has a non-unit probability factor in the initial state, a non-vanishing occupation number in the final state, and non-vanishing overlaps with other Dyson spin-orbitals.
4. The construction (building-up or Aufbau) principles of traditional, uncorrelated, molecular-orbital theory that produce electron densities ascribe unit probability to each occupied spin-orbital in an initial-state, N-electron Slater determinant. To account for electron correlation, a similar process of construction with Dyson spin-orbitals requires the introduction of non-unit probability factors for each electron-binding energy below the chemical potential. These factors correspond to a non-orthogonal set of Dyson spin-orbitals that suffices to reconstruct electron densities. For most closed-shell molecules and ions, pole strengths are close to 0.9 for electron affinities and the first few electron-detachment energies. Somewhat smaller values near 0.8 are usually obtained for the principal, core-electron-detachment energies. Between these relatively simple regions lies the inner-valence spectrum, which typically displays copious final states with low probability factors.

Upon accepting an award named for G. N. Lewis by the California Section of the American Chemical Society, Mulliken in 1960 posed a question that has been interpreted in a variety of ways: What are the electrons really doing in molecules?[137] To many investigators, the terms in this question express a desire to know about the positions, momenta, and energies of electrons understood to be quantum mechanical particles that are subject to Fermi–Dirac statistics and Pauli's principle of exclusion. To the extent that the stationary states of time-independent theory can provide a satisfactory answer to such a question, spin-orbitals associated with electron-binding energies, probabilities of transition between initial and final states, and components of the initial state's electron density provide the most complete description. Dyson spin-orbitals are the foundation of improved Aufbau concepts in which probability factors incorporate correlation effects while respecting anti-symmetrization. In this improved picture of chemical bonding, interacting quantum mechanical systems are described in terms of spin-orbitals with probability factors that correspond to observable transitions.

Table I exhibits a comparison of the Hartree–Fock and Dyson pictures of electronic structure. Dyson spin-orbitals, their probability factors, and electron-binding energies obtained from a correlated one-electron (Dyson quasiparticle) equation supplant the less numerous Hartree–Fock spin-orbitals in building-up or Aufbau procedures for density matrices, electron densities, and total, electronic energies. Probability factors also appear in formulas for transition intensities and sum rules. In the Dyson picture, the Coulomb–exchange (J–K) potential of the canonical, Hartree–Fock equations is improved by the energy-dependent, non-local, self-energy operator, $\Sigma(E)$, in the self-consistent solution of the Dyson quasiparticle equation. The latter operator may be systematically

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improved to the exact limit wherein exact, electron-binding energies and normalized, Dyson spin-orbitals emerge as eigenvalues and eigenfunctions.

COMPARISON OF DYSON AND LOCALIZED SPIN-ORBITALS

For most closed-shell molecules and ions, Koopmans's identity provides qualitatively valid results for the largest electron affinities and the lowest electron-detachment energies. For transitions between open-shell species in which the initial and final states are dominated by a single Slater determinant, canonical, unrestricted Hartree–Fock spin-orbital energies may remain useful to a similar degree when spin contamination is not large. Canonical *orbitals* of restricted, open-shell Hartree–Fock theory that satisfy the Brillouin and Koopmans conditions with respect to configuration-state functions offer a more rigorous alternative that conserves spin quantum numbers.[138–141] (Note that the formal satisfaction of the Brillouin and Koopmans conditions by unrestricted Hartree–Fock spin-orbitals is not identical to the satisfaction of these conditions with respect to configuration-state functions by orbitals in restricted, open-shell Hartree–Fock theory.) In such cases, the self-energy term of Eq. (22) introduces corrections to canonical Hartree–Fock spin-orbital energies that are usually necessary for making convincing spectral assignments. (The order of final states predicted with canonical, Hartree–Fock spin-orbital energies is often incorrect.[94,96,97,142]) Dyson and canonical Hartree–Fock spin-orbitals bear a close resemblance to each other, with the chief difference being the deviation of the correlated, probability factor from its uncorrelated value of unity. Canonical spin-orbitals of closed-shell, Hartree–Fock theory and their correlated, Dyson counterparts have a clear interpretive advantage over localized spin-orbitals for the assignment of electron-binding energies to spectral peaks.

Localized spin-orbitals,[143–145] obtained via unitary transformations of their canonical counterparts, preserve the Hartree–Fock Slater determinant[131] and therefore generate alternative ways of dividing the same electron density with respect to spin-orbital contributions.[146–150] (In calculations on large molecules, localized spin-orbitals also may be employed[17] to increase the efficiency of calculations without adversely affecting the numerical precision or physical significance of the results.) The interpretive advantages of such an alternative basis accrue when a localized property, such as a bond angle or a spin-density at a nuclear position, may be ascribed to a small subset of localized spin-orbitals. Confirmation or generalization of traditional, localized notions of chemical bonding, especially those that pertain to electron pairs, may provide insight into a self-consistent-field determinant. Acceptance of the concept of three-center, two-electron bonds in boranes was abetted by such means.[151] Theoretical characterizations of inorganic clusters increasingly appeal to schemes that partition electron densities according to electron pairs distributed over three or more centers.[152] Valence-shell-electron-pair-repulsion theory,[153,154] a staple of basic, structural-chemistry curricula, has a similar qualitative foundation that resembles the Edmiston–Ruedenberg localization criterion.[145] As with any orbital concept, the utility of localized-orbital concepts rests on their explanatory economy and predictive accuracy. Explanatory economy may be optimized for different audiences depending on their educational traditions and depth of interest in electronic structure. In the best case, predictions based on orbital concepts can stimulate experimentation that can confirm or refute well-defined hypotheses.

Techniques for obtaining localized analyses of electron densities may be extended to incorporate electron correlation. Isopycnic (density-conserving) spin-orbitals obtained with correlated (i.e., non-idempotent) one-electron, reduced-density matrices may be defined by optimization criteria (e.g., those of Boys[143,144] or Edmiston and Ruedenberg[145]) that lead to localized amplitudes.[155] As with Dyson spin-orbitals, these functions form non-orthogonal sets (the linear transformations from natural spin-orbitals are not unitary) with non-integer, occupation numbers that sum to N. Examples include the non-orthogonal orbitals produced in the simplest varieties of generalized, valence-bond theory.[156]

Procedures for obtaining localized orbitals that invoke only the one-electron, reduced-density matrix and an optimization criterion (e.g., the generalized Foster–Boys[144] or Edmiston–Ruedenberg[145] schemes) avoid biased interpretations of chemical bonding that may arise when the one-electron basis or wavefunction *Ansätze* are prepared with a certain result in mind. One-electron properties (e.g., electrostatic potentials and spin densities) may be analyzed in terms of a sum over localized spin-orbital matrix elements of the corresponding operator. Simplified interpretations may be procured when one or a small number of terms dominate the summation. In the absence of such simplicity, the meaning of a single, localized, spin-orbital's expectation value may be obscure, and an appeal to the entire summation over localized spin-orbitals may be required.

Whereas well-defined, localized spin-orbitals are founded on an array of global indices (i.e., the one-electron, reduced-density matrix) of only a single state, Dyson spin-orbitals of electron detachment map onto transitions between an initial, N-electron state and specific final states with N − 1 electrons while retaining their relevance to the properties of the initial state. Summations over both kinds of spin-orbitals may be compared with the results of experimental measurements of one-electron properties and provide uniquely defined ways of deconstructing electron densities. The panoply of electron-spectroscopic methods and scattering experiments that result in electron detachment from a target state provide complementary tests of the predicted Dyson spin-orbitals. Recent measurements on Dyson spin-orbitals have been limited to the lowest, electron-detachment energies. Full reconstruction of the one-electron-density matrix from experiment therefore remains a remote, but attractive, prospect.

CORRELATED, INITIAL-STATE SPIN-ORBITALS

Spin-orbitals that characterize an initial state may be defined in various ways. The elements of the Fock and self-energy matrices that appear in the Dyson quasiparticle equation may be determined completely by reduced-density matrices of the initial state. No appeal to final-state information is required to evaluate $\mathbf{f}$ or $\boldsymbol{\Sigma}(E)$ exactly or in approximate calculations. Dyson spin-orbitals suffice to construct the one-electron, reduced-density matrix of the initial state. Their one-electron expectation values, electron-binding energies, and probability factors appear in total-energy expressions

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that are exact. Experimental techniques that provide information on the amplitudes of Dyson spin-orbitals in position or momentum space continue to multiply. As these methods of observation advance toward transitions of higher energy, the limit of complete reconstruction of the one-electron, reduced-density matrix by experimental means can be approached. The mapping of Dyson spin-orbitals to final states does not diminish their relevance to the electronic structure of an initial state.

Natural spin-orbitals are the most efficient in the reconstruction of the one-electron, reduced-density matrix of an initial state. Electron-binding energies, natural spin-orbitals, and total energies may be related to each other with the extended Koopmans (EK) theorem.[92,157] The lowest electron-detachment energy of a given irreducible representation and spin with respect to a full configuration-interaction energy of the initial state may be approximated by an eigenvalue in a secular equation,

$$\mathbf{f}^{EK}\mathbf{c}^{EK} = \boldsymbol{\rho}\mathbf{c}^{EK}\mathbf{e}^{EK}, \qquad (39)$$

where the elements of the matrix $\mathbf{f}^{EK}$ depend on one-electron and two-electron reduced-density matrices of the initial state and $\boldsymbol{\rho}$ is the former density matrix. The initial state's total energy may be recovered with a summation over natural spin-orbitals (p) according to

$$\langle H\rangle = \frac{1}{2}Trace\left[\mathbf{h}_1\boldsymbol{\rho} + \mathbf{f}^{EK}\right] = \frac{1}{2}\sum_{p}\left[h_{1,pp}n_p^{nat} + f_{pp}^{EK}\right]. \qquad (40)$$

A given, natural spin-orbital and its corresponding, occupation number have no necessary connection to electron-binding energies or transition probabilities. Dyson spin-orbitals that emerge from EK calculations are not equal to natural spin-orbitals and are expressed as linear combinations of them. (The diagonal elements of f^{EK} in the natural basis belonging to a complete-active-space, self-consistent-field wavefunction have been used recently to estimate electron-detachment energies.[80]) Probability factors equal unity only when $\boldsymbol{\rho}$ is idempotent and are less than unity otherwise. Equation (39) is subject to numerical instabilities because the exact, one-electron-density matrix has infinitely many non-zero eigenvalues,[158] most of which will be exceedingly small. Such difficulties can be expected to become more severe with the improvement of basis sets for the description of the initial state. The separate task of describing the EK spin-orbitals[159,160] [which are determined by the eigenvectors of Eq. (39), have vanishing, natural-occupation numbers in their respective, final states, and serve chiefly as probes of long-range decay in density matrices] requires the inclusion of basis functions that are remote from the nuclei and the bulk of the electron density.

Other kinds of initial-state orbitals may be based on localized pictures of chemical bonding that originated with Lewis and Langmuir,[161,162] appeared in quantum mechanical form in the Heitler–London–Slater–Pauling[163–166] theory of valence bonds and its subsequent generalizations,[167–170] and re-emerged from various protocols for the extraction of localized molecular orbitals from single-determinantal or correlated wavefunctions. In *a priori* approaches, a variational *Ansatz* that mathematically expresses a localized orbital concept (e.g., the perfect-pairing, generalized valence bond wavefunction[156]) is optimized with respect to parameters that allow for the variation of orbitals. Such optimizations do not necessarily confirm the original, localized-orbital concepts. For example, recent variational calculations of various kinds of valence-bond wavefunctions for ethylene and acetylene yielded hybridized sp^n orbitals with n very far from the expected values of 2 and 3.[171] In *a posteriori* approaches, reduced-density matrices obtained from many-electron wavefunctions are analyzed in terms of localized concepts. For example, electron densities of correlated wavefunctions may be decomposed into non-orthogonal spin-orbital contributions by performing isopycnic transformations that can employ a variety of localization criteria.[155]

To obtain localized pictures of electronic structure, it is not necessary to appeal to reduced-density matrices or even to orbital concepts. The positions and spins of N electrons that correspond to the global probability maximum of a many-electron wavefunction inevitably generate completely localized representations of electronic structure.[172,173] Averaging procedures that consider other sets of electronic coordinates of high probability are needed for a realistic representation of a specific energy eigenstate that respects the uncertainty principle.[174]

ELECTRON-BINDING ENERGIES

Exact Dyson spin-orbitals are eigenfunctions of the Fock plus self-energy operator in the Dyson quasiparticle equation. Their eigenvalues are exact electron-binding energies. Several kinds of spectra provide independent measurements of these spin-orbital energies and experimental tests, which may confirm or refute predictions based on calculations. Amplitudes and squared moduli of Dyson spin-orbitals also are subject to experimental scrutiny.

Canonical Hartree–Fock spin-orbital energies equal electron-binding energies in zeroth order with respect to the Møller–Plesset fluctuation potential.[93] In zeroth order, Dyson spin-orbitals equal canonical, Hartree–Fock spin-orbitals. Both statements remain true, regardless of the spin-orbital basis (canonical or localized) used to express the zeroth-order counterpart of the operator in the Dyson quasiparticle equation.

As the operator in the Dyson quasiparticle equation approaches the exact case (e.g., in progressively higher orders of the Møller–Plesset fluctuation potential), the resulting electron-binding energies and Dyson spin-orbitals will be unaffected by the choice of basis used to express the f and $\Sigma(E)$ matrices. The Dyson spin-orbitals that typically emerge from these calculations offer a succinct description of an electron detachment and provide a uniquely defined contribution to the initial-state, electron density.

Dyson spin-orbitals of electron attachment are not included in summations that pertain to initial state properties, but they are useful in the interpretation of many kinds of spectroscopic and scattering experiments.[175,176] Bound, final states with N + 1 electrons correspond to Dyson spin-orbitals whose amplitudes approach zero at long distances from the nuclei and electrons of the initial state with N electrons. For most molecules and atoms, there are only a small number of stable anions, and each final state is assigned to a diffuse, Dyson spin-orbital. (It is not unusual for there to be zero bound anions, especially for saturated, non-polar, closed-shell species.) Cationic initial states often have many positive electron affinities, some of which may be associated with the Rydberg series of molecular excited states.[177–183] Marginal cases in which the energy of electron attachment is close to zero may occur for molecules with polar or ionic bonds. Electrostatic potentials in such systems lead to diffuse, Dyson spin-orbitals of electron attachment whose largest absolute amplitudes accumulate near molecular regions of net positive charge. Electron-correlation effects can be decisive in determining the stability of an electron-attached species with respect to an initial state. Stable anions correspond to asymptotically decaying Dyson spin-orbitals, a characteristic that should be verified through basis-set improvements in marginal cases. Caution should be exercised when calculations produce small, negative electron affinities that approach zero with the enlargement of atomic basis sets, for they are likely to yield Dyson spin-orbitals that are projections of continuum functions onto the basis set.

To enable the study of temporary anions, stabilization techniques extend the ambit of unaltered quantum-chemistry technology to the calculation of resonance energies and lifetimes.[176,184,185] Complex absorbing potentials offer an alternative route to these data with relatively minor modifications to standard codes.[186–190] Basis-set quality and improved treatments of correlation effects may affect amplitudes near nuclei and at long range of Dyson spin-orbitals corresponding to electron–molecule resonances.[191,192] Orthogonality relationships between the real and imaginary parts of Dyson spin-orbitals have been illustrated in calculations on several molecules.[193,194]

When applying standard codes to valence, temporary anions, such as π^* resonances in unsaturated organic molecules, considerable care should be exercised in procuring reference spin-orbitals that are qualitatively reasonable. A common pitfall occurs when default options, in combination with large, flexible basis sets, generate highly diffuse, non-valence, reference spin-orbitals, for subsequent, perturbative, many-body calculations are unlikely to yield Dyson spin-orbitals of electron attachment with valence characteristics. Preliminary calculations with few or no diffuse functions often procure better initial guesses for valence, anionic states that may be updated with larger basis sets and correlation methods.

SPIN-ORBITAL UNIQUENESS

Any many-electron wavefunction, exact or approximate, may be used to produce a one-electron, reduced-density matrix. The natural spin-orbitals and their occupation numbers therefore are uniquely defined and more robust than any procedure based on a localization protocol, which may not converge to a unique set of spin-orbitals. Such ambiguities (e.g., σ–π vs banana patterns associated with double bonds, alternative resonance structures) often beset widely used localization methods.[143–145]

Dyson spin-orbitals are defined solely in terms of many-electron states. They have the additional advantage of being physically meaningful not just collectively (as in the case of the natural spin-orbitals), but individually as well. Consider the r–s element of the spin-orbital-density matrix of an initial, N-electron state in an orthonormal spin-orbital basis,

$$\rho_{rs} = \left\langle \Psi_I \middle| a_r^\dagger a_s \Psi_I \right\rangle. \tag{41}$$

Insertion of a complete set of final states with N − 1 electrons with index *F* yields

$$\rho_{rs} = \sum_F{}' \left\langle \Psi_I \middle| a_r^\dagger \Psi_F \right\rangle \langle \Psi_F | a_s \Psi_I \rangle = \sum_F{}' C_{rF}^* C_{sF}. \tag{42}$$

After using Eq. (33), the one-electron, reduced-density operator for the initial state reads

$$\sum_{rs} \chi_r(x) \rho_{rs} \chi_s^*(x') = \sum_F{}' \varphi_F^{Dyson}(x) \left[\varphi_F^{Dyson}(x')\right]^*. \tag{43}$$

One needs only state functions (i.e., Ψ_I and the Ψ_F set) from Hilbert-space methods or eigenfunctions of the Dyson quasiparticle equation to define these spin-orbitals, which may be regarded as Fourier coefficients in the expansion of Ψ_I in terms of the Ψ_F set. No partitioning of direct space or Hilbert space has been postulated. No concepts external to the Schrödinger equation except spin have been introduced.

LOCALIZED DYSON SPIN-ORBITALS

To substitute a set of localized spin-orbitals for Dyson spin-orbitals in Eq. (43), it is necessary to introduce a sum over an alternative set of states with N − 1 electrons that are not eigenfunctions of the many-electron Hamiltonian. In the context of time-independent theory, they may be introduced, for example, to produce an advantageous basis for non-adiabatic, vibronic wavefunctions. This approach may provide more succinct interpretations of photo-detachment spectra when final states with small energy differences induce changes in point-group symmetry.

Time-dependent superpositions of stationary states with N − 1 electrons may correspond to Dyson spin-orbitals that temporally evolve[195] from one localized function to another. Temporally short pulses of light that suffice for production of an evolving, localized Dyson spin-orbital could provide an opportunity to observe amplitudes that conform to notions inherited from introductory textbooks (e.g., lone pairs on water molecules[196]) or to other desired patterns. The design of such optical protocols could also serve to control the reactivity of final states.

The concept of Dyson spin-orbitals is sufficiently capacious as to encompass the delocalized patterns that emerge from traditional, molecular-orbital theory and temporally evolving amplitudes that evoke the localized notions of valence-bond theory. In the former case, the mission of spectroscopy in seeking information on stationary states is served. In the latter case, the goal of point-wise control of the electronic structure and reactivity by optical means is advanced.

DYSON ORBITALS FROM PERTURBATIVE, ELECTRON PROPAGATORS

Perturbative approximations for the self-energy operator in the Dyson quasiparticle equation may be derived from the following expression of the electron propagator matrix:[8,19]

$$\mathbf{G}(E) = (\mathbf{a}^\dagger \,|\, (E\hat{I} - \hat{H})^{-1} \mathbf{a}^\dagger). \tag{44}$$

A column vector of creation operators corresponding to orthonormal spin-orbitals is represented by $\mathbf{a}^\dagger$. The identity and Hamiltonian

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super-operators are defined[19,197] by their actions on elementary field operators or products of them, X, such that

$$\hat{I}X = X, \tag{45}$$

$$\hat{H}X = XH - HX. \tag{46}$$

Matrix elements are evaluated according to an inner product that reads

$$(X\,|\,Y) = \langle 0\,|\,X^\dagger Y + YX^\dagger\,|\,0\rangle \tag{47}$$

in which the N-electron reference state is designated as $|0\rangle$. After introducing an inner projection of the inverse (resolvent) super-operator, one obtains

$$\mathbf{G}(E) = \left[(\mathbf{a}^\dagger\,|\,\mathbf{a}^\dagger)(\mathbf{a}^\dagger\,|\,\mathbf{b})\right]\begin{bmatrix}(\mathbf{a}^\dagger\,|\,(E\hat{I}-\hat{H})\mathbf{a}^\dagger) & (\mathbf{a}^\dagger\,|\,(E\hat{I}-\hat{H})\mathbf{b})\\ (\mathbf{b}\,|\,(E\hat{I}-\hat{H})\mathbf{a}^\dagger) & (\mathbf{b}\,|\,(E\hat{I}-\hat{H})\mathbf{b})\end{bmatrix}^{-1} \times \begin{bmatrix}(\mathbf{a}^\dagger\,|\,\mathbf{a}^\dagger)\\ (\mathbf{b}\,|\,\mathbf{a}^\dagger)\end{bmatrix}, \tag{48}$$

where $\mathbf{b}$ is the vector of products of n creators and (n − 1) annihilators from n = 2 to n = N + 1.[198] This vector encompasses n-particle–(n − 1)-hole (e.g., 2p1h, 3p2h) and n-hole–(n − 1)-particle (e.g., 2h1p, 3h2p) products.

After orthogonalizing the threefold (2h1p and 2p1h) and higher products in $\mathbf{b}$ to the space of simple creators ($\mathbf{a}^\dagger$) and to each other, the matrix expression for the electron propagator reads

$$\mathbf{G}(E) = \left[\mathbf{1}\,\mathbf{0}\right]\begin{bmatrix}E\mathbf{1} - (\mathbf{a}^\dagger\,|\,\hat{H}\mathbf{a}^\dagger) & -(\mathbf{a}^\dagger\,|\,\hat{H})\mathbf{d})\\ -(\mathbf{d}\,|\,\hat{H})\mathbf{a}^\dagger) & E\mathbf{1} - (\mathbf{d}\,|\,\hat{H})\mathbf{d})\end{bmatrix}^{-1}\begin{bmatrix}\mathbf{1}\\ \mathbf{0}\end{bmatrix}, \tag{49}$$

where $\mathbf{d}$ corresponds to the orthogonalized set of product operators.

The poles of the electron propagator are eigenvalues of the super-operator secular equations in the combined space of $\mathbf{a}^\dagger$ and $\mathbf{d}$ operators,

$$\hat{\mathbf{H}}\mathbf{C} = \mathbf{C}\boldsymbol{\epsilon}. \tag{50}$$

The residues (and therefore the Dyson spin-orbitals) are determined by the elements of $\mathbf{C}$ that pertain to the primary operator ($\mathbf{a}^\dagger$) space. ($\mathbf{C}$ also has elements that pertain to the $\mathbf{d}$ operators.) In Eq. (49), only the upper-left block of the inverse matrix survives multiplication by the unit and zero matrices. Elements of the $(\mathbf{a}^\dagger\,|\,\hat{H}\mathbf{a}^\dagger)$ matrix in a general basis of orthonormal spin-orbitals with indices p, q, r, and s read

$$(a_p^\dagger\,|\,\hat{H}a_q^\dagger) = h_{pq} + \sum_{rs}(pq\,||\,rs)\langle 0\,|\,a_r^\dagger a_s\,|\,0\rangle = f_{pq} \tag{51}$$

and constitute a generalized Fock matrix in which the reference state's one-electron-density matrix determines the Coulomb-exchange operator. The inverse of the electron propagator matrix reads

$$\mathbf{G}^{-1}(E) = E\mathbf{1} - \mathbf{f} - \boldsymbol{\Sigma}(E). \tag{52}$$

The energy-dependent, self-energy operator is given by

$$\boldsymbol{\Sigma}(E) = (\mathbf{a}^\dagger\,|\,\hat{H}\mathbf{d})(\mathbf{d}\,|\,(E\hat{I}-\hat{H})\mathbf{d})^{-1}(\mathbf{d}\,|\,\hat{H}\mathbf{a}^\dagger). \tag{53}$$

[Contributions to $\mathbf{f}$ that arise from correlation in $|0\rangle$ are sometimes denominated energy-independent or constant, self-energy terms and are denoted by $\boldsymbol{\Sigma}(\infty)$.] Poles of the electron propagator correspond to zero eigenvalues of $\mathbf{G}^{-1}(E)$ and therefore to self-consistent (with respect to E) eigenvalues in the Dyson quasiparticle equation. Normalized Dyson orbitals are obtained as the corresponding eigenfunctions.

Electron-propagator calculations based on Hartree–Fock reference determinants and renormalized approximations to $\boldsymbol{\Sigma}(E)$ [where non-vanishing, off-diagonal elements in the inverse matrix of Eq. (53) generate terms in all orders of the fluctuation potential] often employ the super-operator secular equation (50) to obtain Dyson spin-orbitals and their transition probabilities. Examples include the algebraic diagrammatic constructions[133,199] in the third (ADC3) and fourth (ADC4) orders and the non-diagonal, renormalized second order[124,125,200] (NR2) method. (Comparisons of the accuracy and computational efficacy of the NR2 and ADC3 methods have appeared recently.[201,202]) A variety of iterative procedures for the diagonalization of large matrices,[203–206] some of which were designed for configuration interaction,[207,208] have been successfully employed in obtaining eigenvalues (i.e., electron-binding energies) that are not subject to any variational bounds.

Calculations on outer-valence, electron-binding energies (e.g., the lowest ionization energies of a closed-shell molecule) that are complete only through second or third order in $\Sigma(E)$ usually yield normalized Dyson orbitals that are dominated by a single canonical, Hartree–Fock component and probability factors above 0.85.[209] Such results provide justification for neglect of off-diagonal elements of $\boldsymbol{\Sigma}(E)$ in the canonical spin-orbital basis. In diagonal-self-energy approximations, the Dyson quasiparticle equation is reduced to an especially simple form where a self-energy correction to a canonical orbital energy typically requires only two or three iterations with respect to E,

$$E = \epsilon_p^{CMO} + \Sigma_{pp}(E). \tag{54}$$

The family of diagonal (also known as quasiparticle) methods includes the second-order (D2), third-order (D3), outer-valence-Green-function (OVGF),[121,210–212] partial-third-order (P3),[213,214] partial-fourth-order (P4),[215–218] and renormalized-partial-third-order (P3+)[124,219] approximations. These methods have enjoyed widespread success even when differences between Koopmans's results (i.e., ϵ^{CMO} values) are small for spin-orbitals that correspond to the same irreducible representation. For example, the P3+ method for electron-detachment energies from closed-shell molecules and anions generates mean unsigned errors of 0.1 eV–0.2 eV with algorithms that have a smaller fifth-power arithmetic scaling factor than that of the electron-repulsion-integral transformation to the molecular-orbital basis.[201,202] Composite models that take advantage of the approximate additivity of basis-set and correlation effects employ large basis sets in D2 calculations that have third-power arithmetic scaling and P3+ results generated with relatively small basis sets.[220] The D2 method has served as a template for several methods that employ semi-empirical Hamiltonians or that introduce parameters for the same-spin and opposite-spin terms in the energy-dependent self-energy.[221–225]

Diagonal methods constrain Dyson spin-orbitals to be products of a canonical, Hartree–Fock spin-orbital and the square root of the probability factor,

$$\varphi^{Dyson}(x) = P^{0.5}\phi^{CMO}(x). \tag{55}$$

D2 and D3 self-energies evaluated with $E = \epsilon_p^{CMO}$ are identical to the terms generated by Rayleigh–Schrödinger perturbation theories (RSPT) of the same orders.[126,127,226] Final-state orbital relaxation and correlation terms and initial-state correlation terms in the diagonal elements of $\boldsymbol{\Sigma}(E)$ have been identified through third order.[19,227] These properties of the simplest diagonal methods describe electron detachment or attachment in terms of a Dyson spin-orbital that remains unaltered by many-body effects, except for a reduction in its probability factor. Pair correlation energies in the N-electron reference state are subtracted or added in final states described with frozen spin-orbitals.

A perturbative analysis of the eigenvalues and eigenvectors that emerge from the super-operator secular equation (50) reveals the common origin of these outcomes. The zeroth-order equation defined in terms of the Møller–Plesset partitioning of the Hamiltonian recovers Koopmans's identity in E_0 and a corresponding unit vector (with its non-zero element in the $\mathbf{a}^\dagger$ space) for C_0,

$$\hat{\mathbf{H}}_0\mathbf{C}_0 = \mathbf{C}_0\mathbf{E}_0. \tag{56}$$

It is easily shown that $E_1 = \mathbf{C}_0^\dagger\hat{\mathbf{H}}_1\mathbf{C}_0$. The first-order correction to the eigenvector reads

$$\mathbf{C}_1 = (E_0\mathbf{1} - \hat{\mathbf{H}}_0)^{-1}\hat{\mathbf{H}}_1\mathbf{C}_0. \tag{57}$$

The first-order super-operator matrix elements between the $\mathbf{a}^\dagger$ and $\mathbf{d}$ spaces are confined to 2p1h and 2h1p (triple) operators. Because couplings between $\mathbf{a}^\dagger$ operators vanish in first order, only 2p1h and 2h1p elements appear in $\mathbf{C}_1$. Therefore, the Dyson spin-orbital remains proportional to a canonical Hartree–Fock spin-orbital, but with a diminished probability factor. The second-order electron binding energy,

$$E_2 = \mathbf{C}_0^\dagger\hat{\mathbf{H}}_1\mathbf{C}_1, \tag{58}$$

is identical to the RSPT result of the same order. In the second-order correction to the eigenvector,

$$\mathbf{C}_2 = (E_0\mathbf{1} - \hat{\mathbf{H}}_0)^{-1}\hat{\mathbf{H}}_2\mathbf{C}_0 + (E_0\mathbf{1} - \hat{\mathbf{H}}_0)^{-1}\hat{\mathbf{H}}_1(E_0\mathbf{1} - \hat{\mathbf{H}}_0)^{-1}\hat{\mathbf{H}}_1\mathbf{C}_0, \tag{59}$$

there are non-vanishing elements in the $\mathbf{a}^\dagger$, triple and quintuple spaces. Here for the first time, there are terms that do not reduce the probability factor and that correspond to non-diagonal self-energies. Now the Dyson spin-orbital is expressed in terms of all the canonical, Hartree–Fock spin-orbitals instead of just one. Although $\mathbf{C}_2$ appears in the first term of the following expression for the third-order energy correction:

$$E_3 = \mathbf{C}_0^\dagger\hat{\mathbf{H}}_1\mathbf{C}_2 + \mathbf{C}_0^\dagger\hat{\mathbf{H}}_2\mathbf{C}_1 + \mathbf{C}_0^\dagger\hat{\mathbf{H}}_3\mathbf{C}_0, \tag{60}$$

the effects of quintuple and non-Koopmans $\mathbf{a}^\dagger$ operators are canceled by the sparsity of $\hat{\mathbf{H}}_1$. Potential instabilities in the first term of the $\mathbf{C}_2$ expression due to small denominators are rendered irrelevant.

These results indicate that attempts to extend diagonal approximations beyond third order may encounter difficulties, for corrections arising from non-diagonal self-energies may be of the same magnitude as those that pertain to triple and quintuple operators. The most successful diagonal methods (such as P3+[124,125] and OVGF[121,211]) that surpass D3 confine themselves to higher-order terms that arise from simple ($\mathbf{a}^\dagger$) and triple operators. Endowed with a convenient compromise of efficiency and accuracy, they have been extensively applied to a variety of molecules, anions, and clusters.[94,97,142,214]

Convenient alternatives to the Hartree–Fock spin-orbital basis that reflect the presence of stronger correlation effects can be supplied by Brueckner determinants. The chief modification in the super-operator Hamiltonian matrix that follows from this choice is the presence of non-zero, occupied-virtual Fock matrix elements. Diagonalization of the occupied–occupied and virtual–virtual blocks of the Fock matrix (i.e., production of semi-canonical or pseudo-canonical orbitals) results in algorithms that have only minor changes with respect to their antecedents that are based on canonical, Hartree–Fock spin-orbitals. The Brueckner-doubles (BD), coupled-cluster method[228] is a useful generator of spin-orbitals in cases where reference–state correlation is relatively strong. The BD, triple-field-operator (or BD-T1) approximation[229–233] of the electron propagator has proven to be a versatile tool for calculations on core ionization energies, on valence electron detachment energies of closed-shell molecules and anions, and on species with diffuse or biradical character. A Dyson spin-orbital in the latter cases can be dominated by a single Brueckner spin-orbital, whereas its expansion in terms of Hartree–Fock orbitals displays several significant components.

DYSON SPIN-ORBITALS FROM RELATED TECHNIQUES

For reference states with multiconfigurational character that is imposed by the unpairing of electrons or by symmetry, several generalizations have been introduced in electron-propagator methodology.[234–239] Multiconfigurational, spin-tensor, electron-propagator (MCSTEP) calculations[237–239] usually employ a complete-active-space, self-consistent-field wavefunction[240,241] as a reference state and an operator manifold that consists of products of N-electron, ket–bra excitation operators with simple or triple field operators. MCSTEP methods have been applied to a variety of small open-shell or diradicaloid molecules and have produced electron binding energies of accuracy comparable to the results obtained with multi-reference wavefunctions.[242–245] These works contain little discussion of the Dyson spin-orbitals that were produced thereby.

A variety of many-body methods that employ initial-state and final-state wavefunctions also produce Dyson spin-orbitals. In equation-of-motion, coupled-cluster theory, a similarity-transformed Hamiltonian obtained via an initial-state calculation is diagonalized in a basis of determinants with N ± 1 electrons.[15,246–251] In the usual formulation, the Hamiltonian matrix is non-Hermitian, and therefore, left and right eigenvectors that are not adjoints of each other are produced. Therefore, only the squared moduli of the corresponding Dyson spin-orbitals are well defined. (There is also no guarantee that the eigenvalues are real; this potential problem appears not to be encountered in practice.) The stationarity of the

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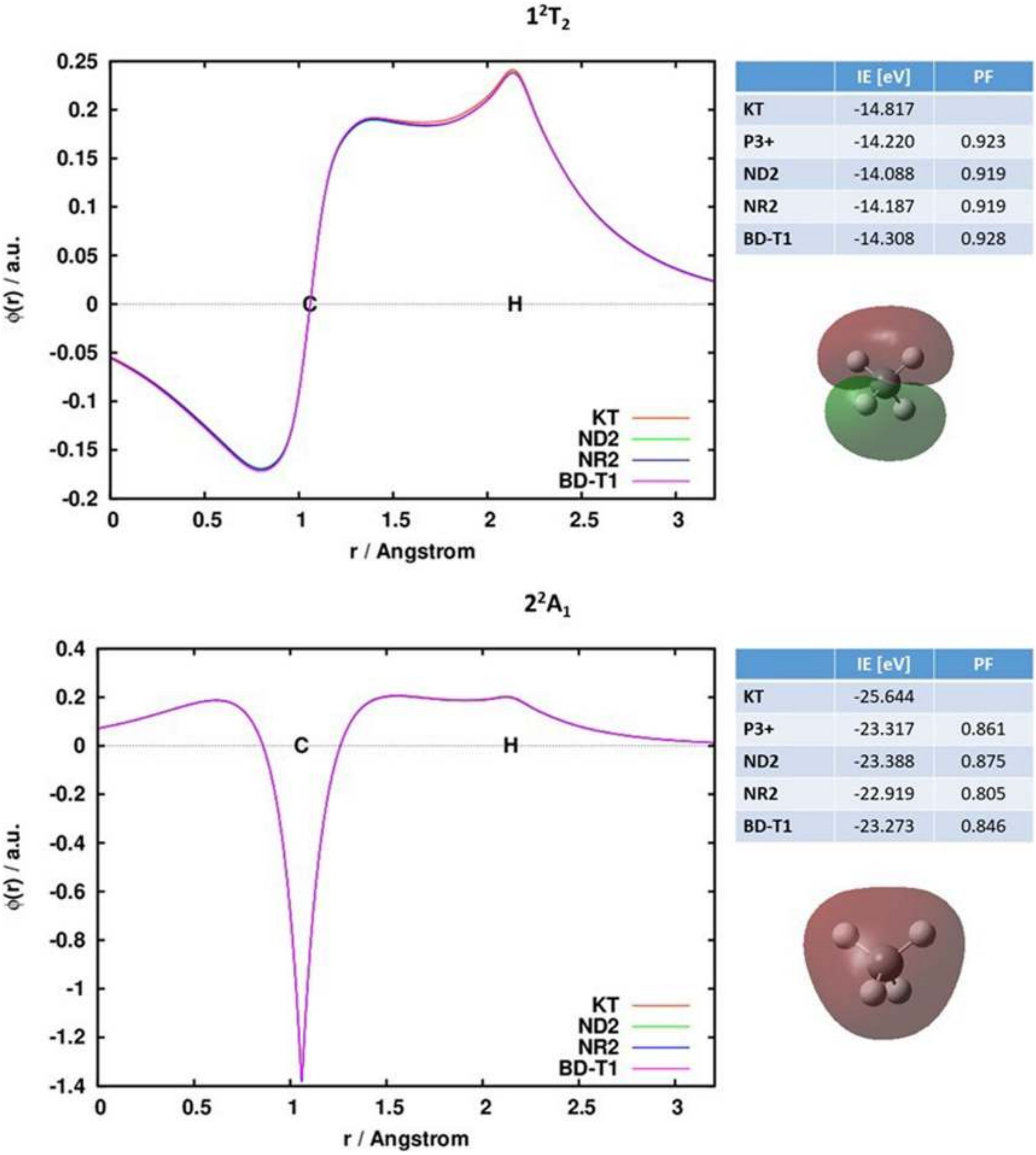
effective Hamiltonian enables decoupled consideration of final states with N + 1 or N − 1 electrons and therefore generates final-state wavefunctions whose overlaps with initial-state wavefunctions yield Dyson spin-orbitals.

Another many-body approach that also decouples electron attachments from detachments constructs an effective Hamiltonian matrix in the determinant spaces of N + 1 or N − 1 electrons. In the non-Dyson electron propagator methods,[108,252–255] the electron-attachment and electron-detachment terms of Eq. (34) are considered separately. The matrix that is diagonalized is Hermitian, and the Dyson spin-orbitals are well-defined. Wavefunctions for the final states are available for the evaluation of final-state properties.[252]

NUMERICAL EXAMPLES

Normalized Dyson spin-orbitals calculated at the uncorrelated (Koopmans's theorem or KT) level of theory are presently compared



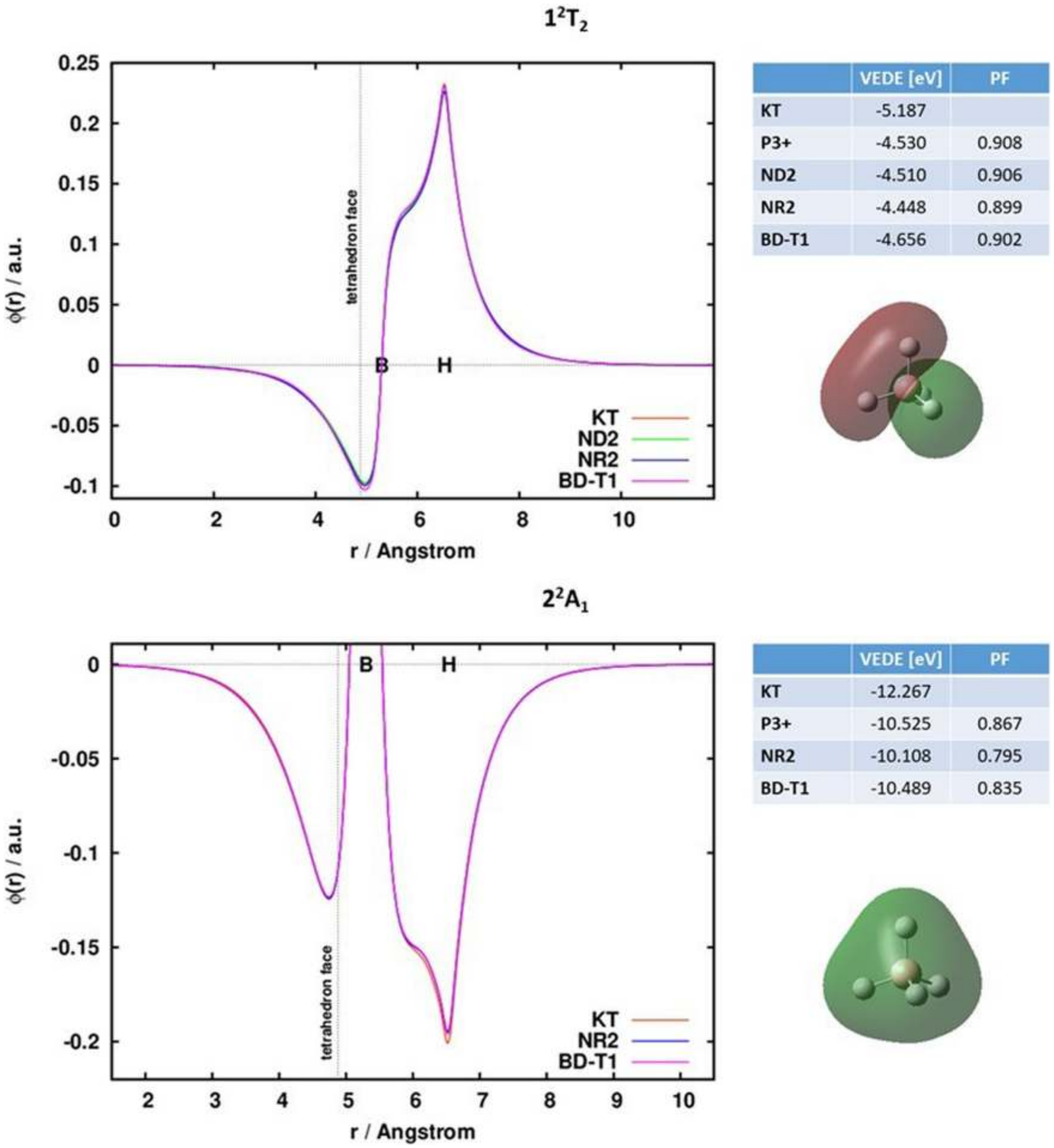
	IE [eV]	PF
KT	-14.817	
P3+	-14.220	0.923
ND2	-14.088	0.919
NR2	-14.187	0.919
BD-T1	-14.308	0.928

	IE [eV]	PF
KT	-25.644	
P3+	-23.317	0.861
ND2	-23.388	0.875
NR2	-22.919	0.805
BD-T1	-23.273	0.846

FIG. 1. Radial plots of Dyson orbitals along a C–H bond of methane, their corresponding ionization energies (IEs), and their probability factors (PFs) for the 1^2T_2 and 2^2A_1 final states of CH_4^+ calculated with various electron propagator methods, the aug-cc-pVTZ basis, and a bond distance of 1.0899 Å. The iso-surfaces of the normalized Dyson orbitals are practically identical.

to those obtained with non-diagonal second order (ND2), NR2, and BD-T1 self-energies. (These calculations were executed with the development version of Gaussian,[256] and figures were generated with Multiwfn,[257] Gnuplot,[258] and GaussView.[259]) In ND2 and NR2 calculations, Dyson spin-orbitals are obtained from the eigenvectors of the super-operator secular equations in the form of linear combinations of canonical, Hartree–Fock spin-orbitals. In BD-T1 calculations, the Dyson spin-orbitals are expressed as linear combinations of pseudo-canonical Brueckner orbitals.

Figure 1 shows that Dyson orbitals of the lowest, ionization energies of methane calculated in various approximations are nearly identical for the $^2T_2$ and $^2A_1$ final states of the methane cation. The aug-cc-pVTZ basis[260] is employed; the C–H distance, optimized with the coupled-cluster single, double, and perturbative triple method [CCSD(T)],[261] is 1.0899 Å. In the former case, amplitudes along a C_3 axis have extrema near the hydrogen nuclei and can be regarded as a pattern of constructive interference between carbon 2p and hydrogen 1s functions. A similar conclusion that involves the



	VEDE [eV]	PF
KT	-5.187	
P3+	-4.530	0.908
ND2	-4.510	0.906
NR2	-4.448	0.899
BD-T1	-4.656	0.902

	VEDE [eV]	PF
KT	-12.267	
P3+	-10.525	0.867
NR2	-10.108	0.795
BD-T1	-10.489	0.835

FIG. 2. Radial plots of Dyson orbitals along a B–H bond of BH_4^-, corresponding vertical electron detachment energies (VEDEs), and their probability factors (PFs) for the 1^2T_2 and 2^2A_1 final states of BH_4 calculated with various electron propagator methods, the d-aug-cc-pVTZ basis, and a bond distance of 1.2397 Å. The iso-surfaces of the normalized Dyson orbitals are practically identical.

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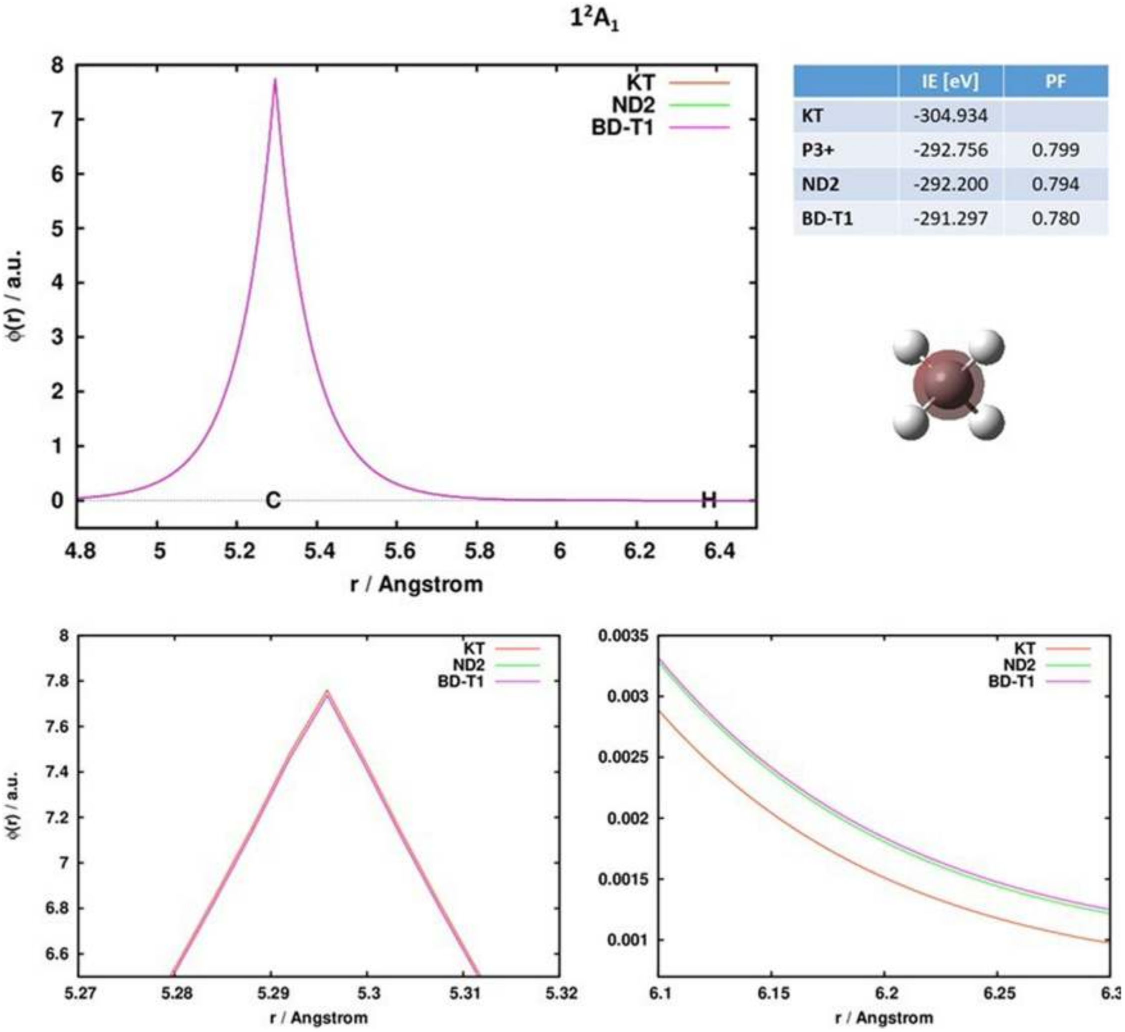
carbon 2s function follows for the $^2A_1$ final state's Dyson orbital. The chief deficiency of the canonical, Hartree–Fock orbitals is their unit probability factors. Occupied, canonical, Hartree–Fock orbitals are usually excellent approximations to correlated, normalized Dyson orbitals for the lowest ionization energies of closed-shell molecules. Exposure of this orbital to the self-energy of the Dyson quasiparticle equation yields an improved, vertical, ionization energy that is closer to experiment [14.4 eV is the maximum of a broad peak[262] that is in close agreement with the ΔCCSD(T) result of 14.37 eV obtained with the same basis] than the KT prediction for the lowest ionization energy. A similar predictive quality is attained for the $^2A_1$ final state, where the BD-T1 result exceeds the ΔCCSD(T) value by 0.08 eV. The probability factor of 0.9 is larger for the first ionization energy than for the second, inner-valence value of 0.85.

Similar conclusions follow for the Dyson orbitals of electron detachment from the isoelectronic anion, BH_4^-. As with methane, closed-shell, canonical Hartree–Fock orbitals bear a close resemblance to correlated, normalized Dyson orbitals, which differ from their uncorrelated counterparts chiefly in their probability factors. (A lack of convergence in the ND2 calculation on the second electron detachment energy is responsible for the absence of a corresponding curve in Fig. 2.) These results were obtained with the d-aug-cc-pVTZ basis and a bond distance of 1.2397 Å. Probability factors for the first electron detachment energy are larger than those for the second. The lowest, vertical, electron-detachment energies calculated with the correlated approximations are in excellent agreement with a basis-set extrapolated value obtained with the CCSD(T) method, 4.68 eV.[202]

Normalized Dyson orbitals for the carbon 1s ionization energy of methane are compared in Fig. 3. The radial plots are nearly indistinguishable, but probability factors of only 0.8 are obtained in ND2 and BD-T1 calculations. (These results are typical for 1s



	IE [eV]	PF
KT	-304.934	
P3+	-292.756	0.799
ND2	-292.200	0.794
BD-T1	-291.297	0.780

FIG. 3. Radial plots of Dyson orbitals along a C–H bond of CH_4, corresponding core-ionization energies (IEs), and their probability factors (PFs) for the core-ionized, $^2A_1$ final state of CH_4^+ calculated with various electron propagator methods, the aug-cc-pCV5Z basis (all electrons correlated), and a bond distance of 1.0899 Å. The ordering of the radial plots in the proximity of the C atom (enlarged in the bottom left panel) is opposite to that in the long-range region (enlarged in the bottom right panel).

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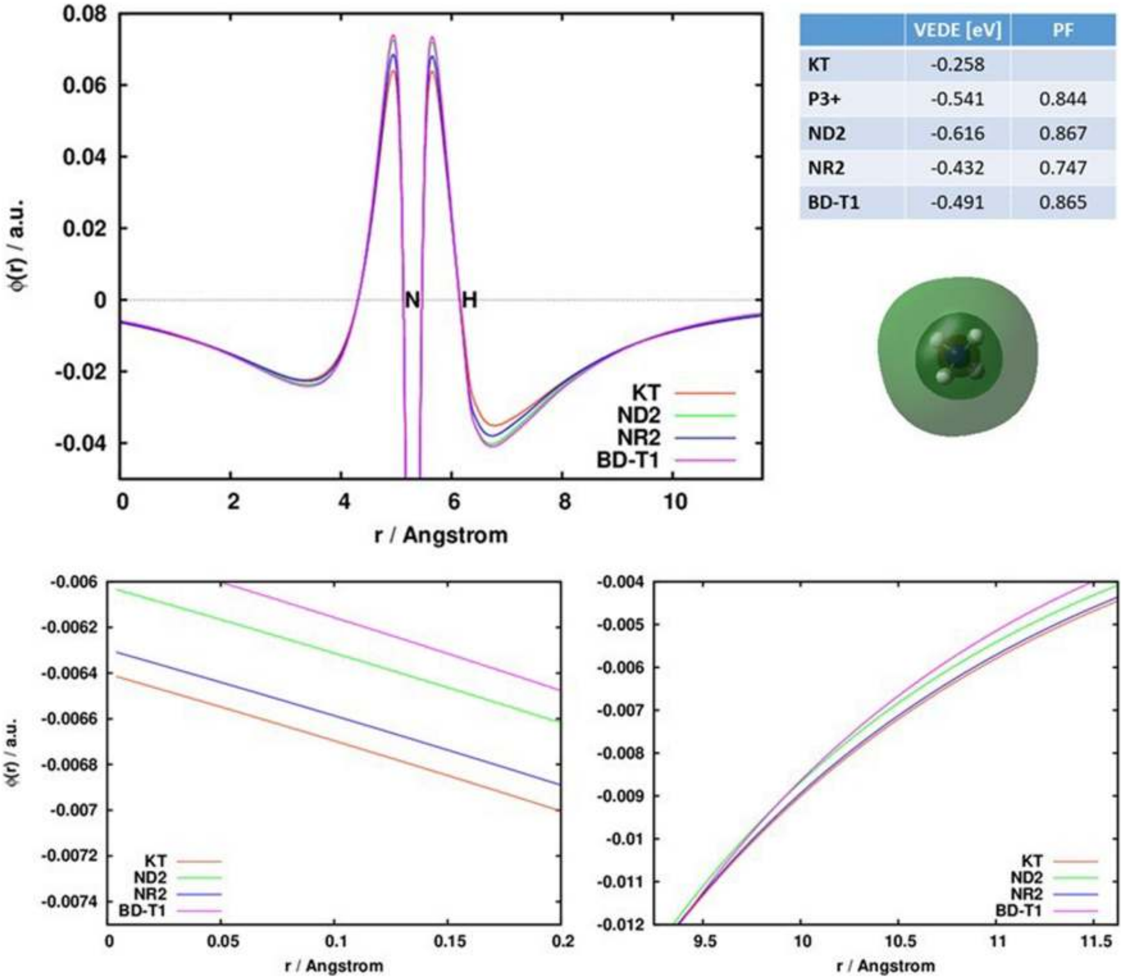
ionization energies of closed-shell molecules.[233]) A closer examination of amplitudes near the carbon nucleus discloses a slightly larger concentration there by the Hartree–Fock orbital. The tendency to spread the amplitudes away from the nucleus by the correlated Dyson orbitals is greater for ND2, which, in general, exaggerates correlation effects, than for BD-T1. The present ionization energies may be increased with a relativistic correction of approximately 0.05 eV that is based on the calculated total energies of two-electron, atomic cations.[233,263] After this update, the BD-T1 ionization energy is only 0.2% larger than the experimental value, 290.91 eV.[264] Most of the corrections to the Koopmans result are captured with diagonal (P3+) or simple non-diagonal (ND2) self-energy approximations. The chief deficiency of uncorrelated theory lies not in its approximation to the normalized Dyson orbital, but in the absence of the energy-dependent, self-energy operator, which is responsible for describing orbital relaxation in final states and consequent reductions in probability factors.

A strongly correlated pair of diffuse electrons in the tetrahedral (double-Rydberg[265,266]) isomer of NH_4^- produces significant differences in Dyson orbitals that result from the four approximations (see Fig. 4). The d-aug-cc-pVTZ basis was used; the optimized N–H distance was 1.0411 Å. Perturbative improvements over KT results that are included in ND2 and NR2 calculations diminish extrema that occur in the internuclear region and amplify those just beyond the protons on C_3 axes. In BD-T1 calculations, employment of more renormalized terms in the self-energy accentuates these trends. This approximation produces the most rapidly decaying, long-range tail in the Dyson orbital. Similar trends are seen along C_2 axes of symmetry. Two radial nodes foreshadow the united-atom limit, wherein the present Dyson orbital approaches a 3s function of Na^-. The two minima result chiefly from interference between a non-valence (3s) function on the nitrogen nucleus and diffuse s functions on the hydrogen nuclei. Most of the electron density that corresponds to these Dyson spin-orbitals lies outside the ammonium



	VEDE [eV]	PF
KT	-0.258	
P3+	-0.541	0.844
ND2	-0.616	0.867
NR2	-0.432	0.747
BD-T1	-0.491	0.865

FIG. 4. Radial plots of Dyson orbitals along a N–H bond of NH_4^-, corresponding vertical electron detachment energies (VEDEs), and their probability factors (PFs) for the $^2A_1$ final state of NH_4 calculated with various electron propagator methods, the d-aug-cc-pVTZ basis and a bond distance of 1.0411 Å. Radial plots in the long-range region are enlarged in the two bottom panels.

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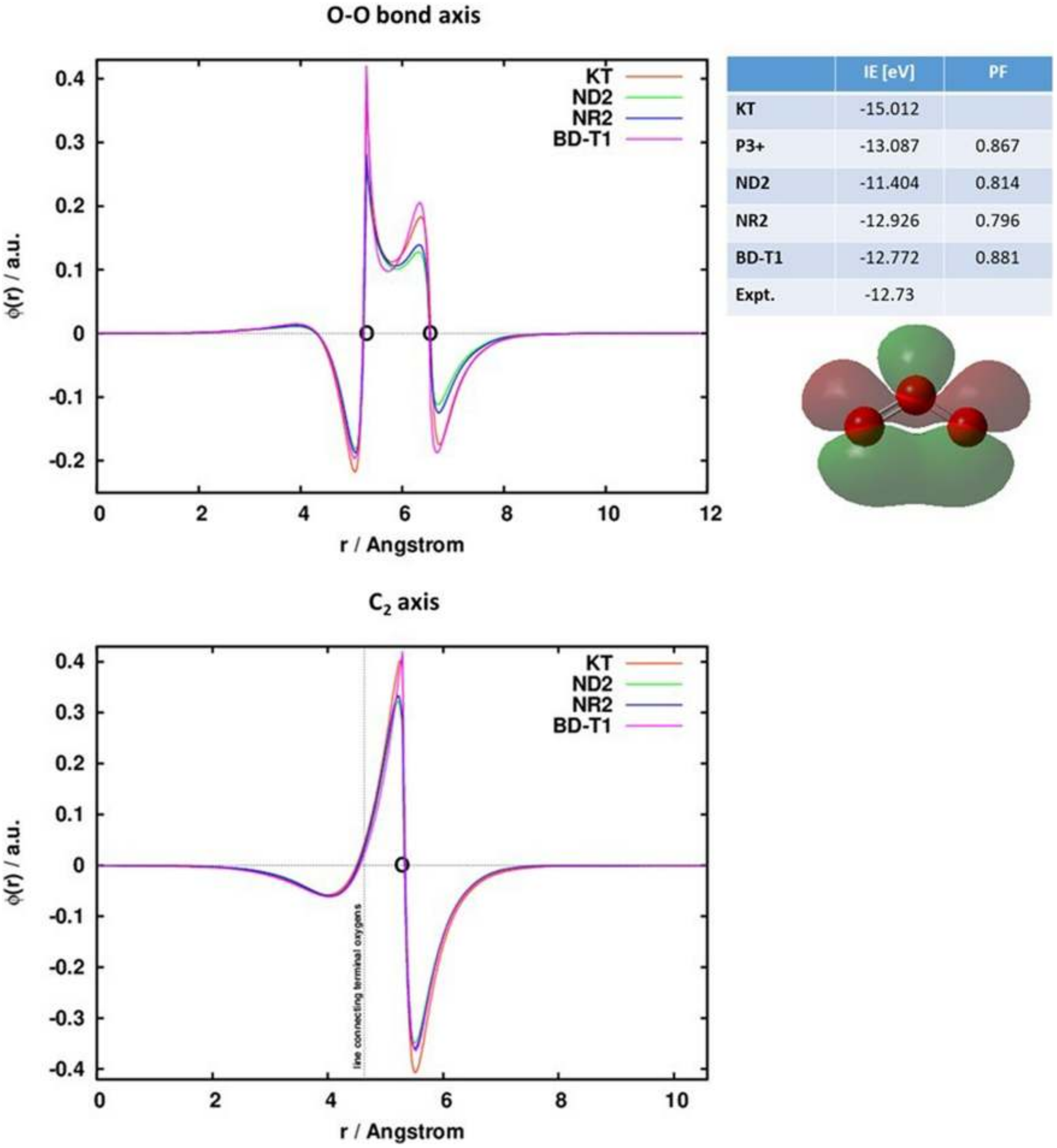
core. The BD-T1 method succeeds in obtaining an accurate electron detachment energy (experiment = 0.47 eV[267,268]) and a probability factor that lies between 0.85 and 0.90.

Differences between Hartree–Fock and correlated amplitudes of normalized Dyson orbitals are even more pronounced in ozone, a molecule with appreciable diradical character.[195,231] In Fig. 5, the results for the $^2A_1$ final state of the ozone cation are displayed. Absolute values of Hartree–Fock amplitudes along the O–O internuclear and C_2 axes contrast with those of normalized Dyson orbitals obtained with the correlated methods. ND2 amplitudes differ most from their Hartree–Fock counterparts. NR2 results differ less, and BD-T1 amplitudes differ least. At long distances from the nuclei, Hartree–Fock orbitals decay most rapidly, followed by BD-T1, NR2, and ND2. Corrections to the Koopmans prediction for the ionization energy are overestimated by ND2. P3+ and NR2 suffice to overcome most of the remaining errors of ND2. The BD-T1 prediction is in excellent agreement with experiment[269] and produces a probability factor of 0.9. An improved description of the normalized Dyson



	IE [eV]	PF
KT	-15.012	
P3+	-13.087	0.867
ND2	-11.404	0.814
NR2	-12.926	0.796
BD-T1	-12.772	0.881
Expt.	-12.73	

FIG. 5. Radial plots of Dyson orbitals along an O–O bond (upper panel) and the main C_2 axis (lower panel) of ozone, corresponding ionization energies (IEs), and their probability factors (PFs) for the $^2A_1$ final state of $O_3{}^+$ calculated with various electron propagator methods, the aug-cc-pVQZ basis, a bond distance of 1.263 Å, and a bond angle of 117.4°. Expt. denotes an experimental result obtained from a photoelectron spectrum.[269]

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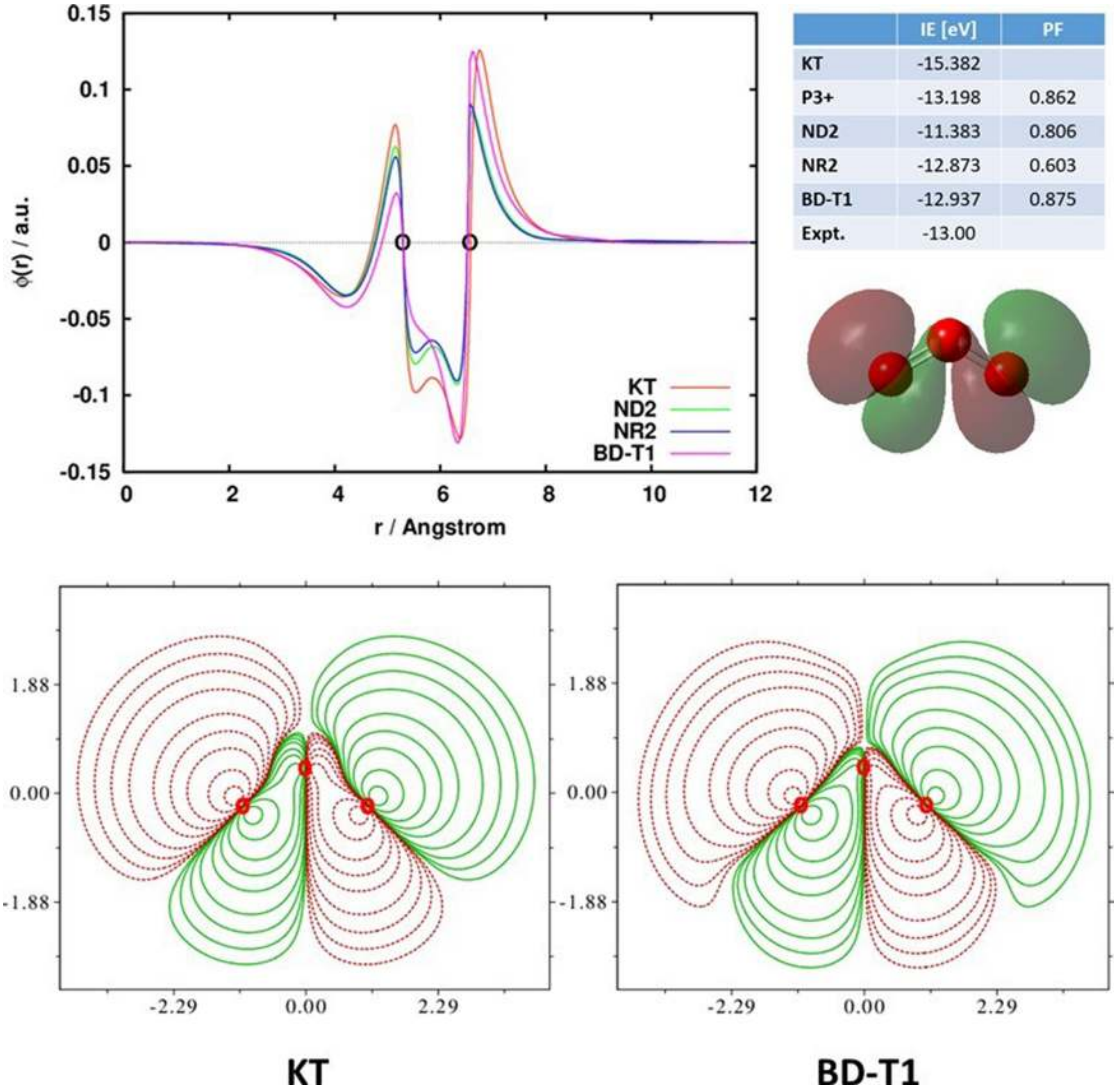
orbital, its energy, and its probability factor result from employment of the renormalized BD-T1 self-energy.

Dyson orbitals for the $^2B_2$ final state in Fig. 6 have even more obvious differences. As in the $^2A_1$ state, the Hartree–Fock amplitudes have greater absolute values in the O–O bond regions. The ND2 and NR2 contours diminish the depth of one of the internuclear minima produced with Hartree–Fock, and BD-T1 eliminates it entirely. Correlation decreases absolute amplitudes and changes the positions of nodes near the central nucleus. It also produces more diffuse outer contours beyond the terminal nuclei. ND2 overcorrects the Koopmans prediction for the ionization energy. NR2 and BD-T1 are in close agreement with the experimental value, but the probability factor for NR2 is too low. The BD-T1 calculation produces a probability factor near 0.9 and is in excellent agreement with the experimental peak.[269] For the first two ionization energies, the most important self-energy terms pertain to electron correlation in final states wherein the removal of an electron from a σ orbital provokes a compensating accumulation of π electrons near the terminal oxygen nuclei.

The next ionization energy of ozone corresponds to a $^2A_2$ state; the Dyson orbitals (Fig. 7) exhibit a π pattern generated by 2p functions with opposite phases on the terminal nuclei. BD-T1 Dyson orbitals are more diffuse than their Hartree–Fock counterparts. All of the methods produce reasonable ionization energies with



	IE [eV]	PF
KT	-15.382	
P3+	-13.198	0.862
ND2	-11.383	0.806
NR2	-12.873	0.603
BD-T1	-12.937	0.875
Expt.	-13.00	

FIG. 6. Radial and two-dimensional plots of Dyson orbitals along an O–O bond and in the molecular plane of ozone, corresponding ionization energies (IEs), and their probability factors (PFs) for the $^2B_2$ final state of O_3^+ calculated with various electron propagator methods, the aug-cc-pVQZ basis, a bond distance of 1.263 Å and a bond angle of 117.4°. Expt. denotes an experimental result obtained from a photoelectron spectrum.[269]

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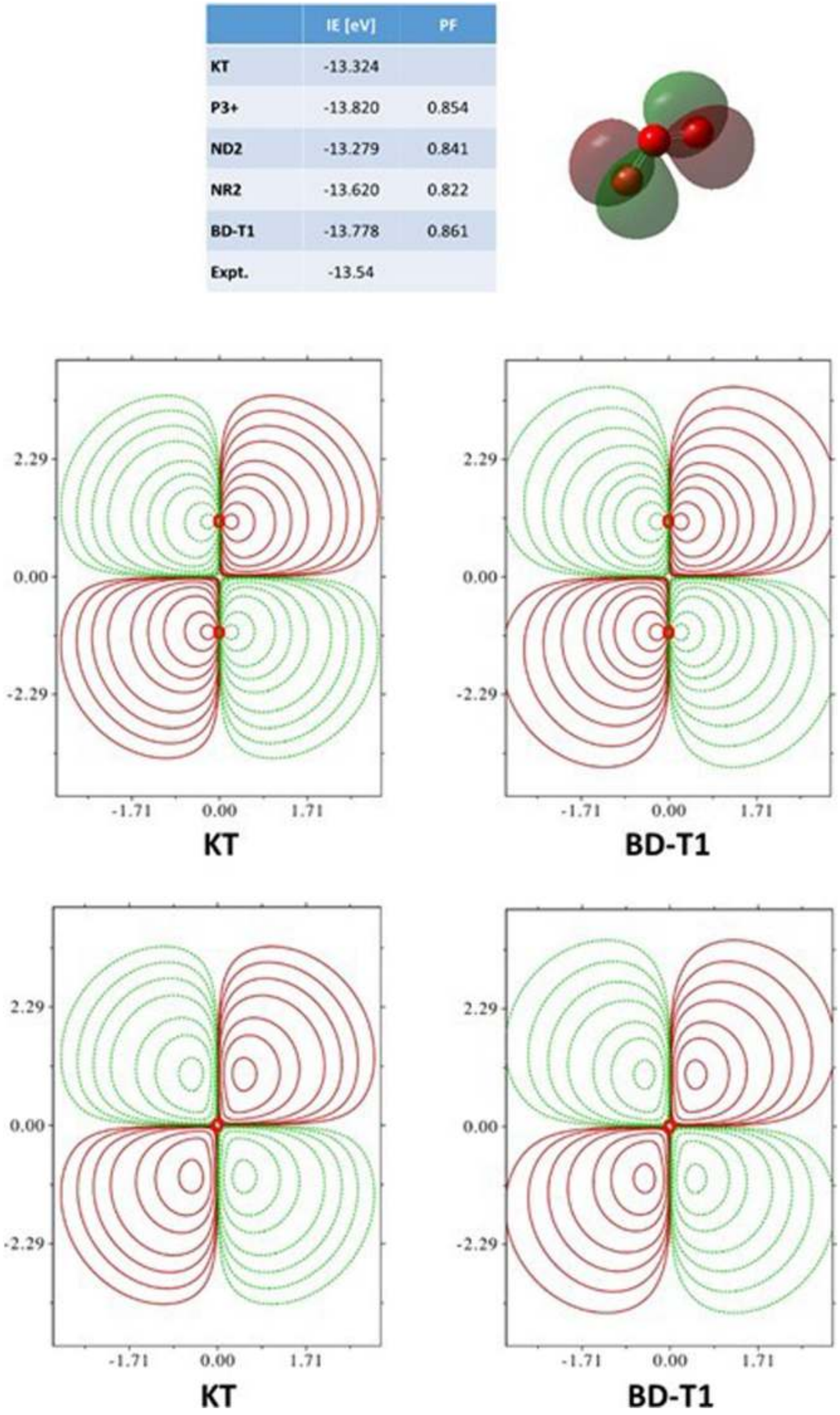
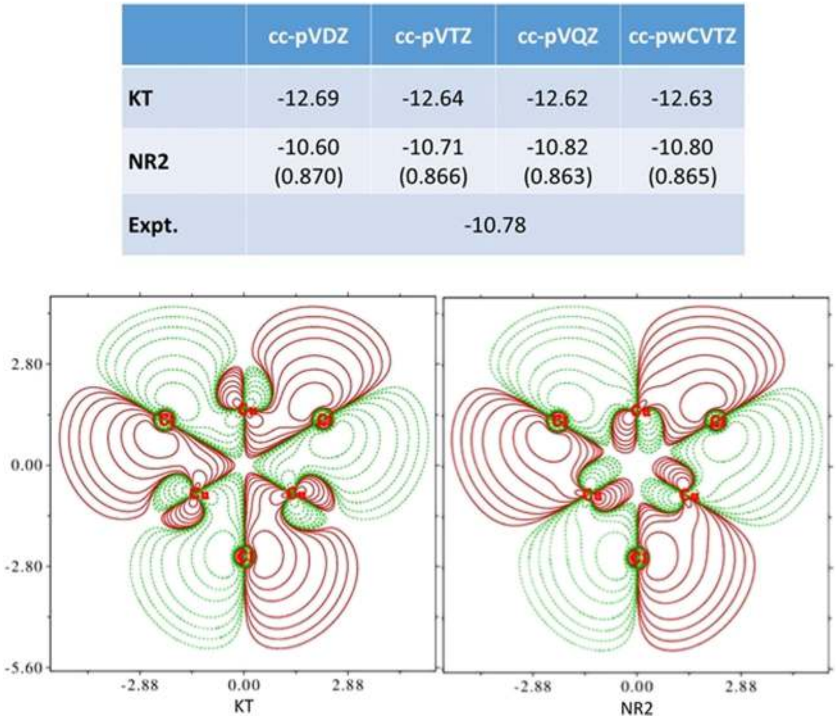
respect to experiment[269] and probability factors near 0.85. The most prominent self-energy terms pertain to initial-state correlation of π electrons that accentuates diradical character and to relaxation of electrons in b_1 orbitals that moves electron density from the central to the terminal nuclei. The corresponding effects on the ionization energy have opposite signs, and therefore, the total correction to the Koopmans result is not as large as in the two other cases where there are σ Dyson orbitals.



	IE [eV]	PF
KT	-13.324	
P3+	-13.820	0.854
ND2	-13.279	0.841
NR2	-13.620	0.822
BD-T1	-13.778	0.861
Expt.	-13.54	

FIG. 7. Dyson orbitals of ozone, corresponding ionization energies (IEs), and their probability factors (PFs) for the $^2A_2$ final state of O_3^+ calculated with various electron propagator methods, the aug-cc-pVQZ basis, a bond distance of 1.263 Å, and a bond angle of 117.4°. Dyson orbitals are plotted in the plane perpendicular to the plane of the nuclei and containing the two terminal oxygen atoms (middle panel) and in the parallel plane that contains the central oxygen (lower panel). Expt. denotes an experimental result obtained from a photoelectron spectrum.[269]



	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pwCVTZ
KT	-12.69	-12.64	-12.62	-12.63
NR2	-10.60 (0.870)	-10.71 (0.866)	-10.82 (0.863)	-10.80 (0.865)
Expt.	-10.78			

FIG. 8. Dyson orbitals of D_{3h} Cu_3Cl_3, corresponding ionization energies (IEs), and their probability factors (PFs) for the $^2A_2'$ final state calculated with Koopmans's theorem (KT) and NR2 electron propagator methods, the cc-pVDZ basis, a Cu–Cl bond distance of 2.207 Å, and a Cu–Cl–Cu bond angle of 75°. Expt. denotes an experimental result obtained from a photoelectron spectrum.[285]

Such differences in the magnitudes of correlation effects with respect to final states are typical of molecules in which there is a low-lying Dyson orbital for the electron affinity with π characteristics. Because ozone has a bound, $^2B_1$ anion, triple-field operators that involve virtual b_1 orbitals are important in describing cationic, final states that correspond to σ Dyson orbitals.[231] Similar responses of electrons in π orbitals to a σ vacancy occur in N_2, heterocyclic compounds, and many other molecules[270–281] and are often responsible for the failure of Koopmans's results to produce the correct order of final states.

Transition-metal complexes often have occupied, canonical, Hartree–Fock orbitals that differ markedly from Dyson orbitals of ionization energies calculated with correlated methods.[282–284] A convincing assignment of the lowest peaks in the photoelectron spectrum[285] of the D_{3h} Cu_3Cl_3 cluster can be obtained with NR2/cc-pvdz,[200,286,287] electron-propagator calculations. A CCSD(T)/cc-pvdz optimization produces a Cu–Cl bond length (2.205 Å) in close agreement with that of a previous computational study (2.207 Å);[288] MP2 frequencies confirm the D_{3h} minimum. Canonical, Hartree–Fock orbitals are in agreement with those of previous calculations[288] to within a few hundredths of an eV. Four, predicted, vertical, ionization energies of 9.72 eV, 10.13 eV, 10.60 eV, and 11.39 eV, respectively, for the $^2E'$, $^2E''$, $^2A_2'$, and $^2A_2''$ final states are in reasonable agreement with the reported spectral features (9.52 eV, 9.64 eV, 10.01 eV, 10.19 eV, 10.78 eV, and 11.25 eV) and their pole strengths vary between 0.87 and 0.89. (The first two pairs of features are associated with degenerate final states that are subject to Jahn–Teller distortions.) Whereas the normalized Dyson orbitals for the $^2E'$ and $^2E''$ final states are composed almost entirely of a single, canonical, Hartree–Fock orbital, significant mixing between two, canonical, Hartree–Fock orbitals occurs in each of the Dyson orbitals for the $^2A_2'$ and $^2A_2''$ final states. In the normalized, a_2' Dyson orbital, the fifth highest, canonical, Hartree–Fock orbital has a coefficient of only 0.79. Amplitudes associated with Cu basis functions are accentuated by the self-energy. In the Hartree–Fock orbital, constructive interference between Cu 3d and Cl 3p functions occurs in the interior of the cluster, but the Dyson orbital calculated with the NR2 method displays a reversal of the Cu 3d phases (see Fig. 8). Antibonding phase relationships between Cu centers are strengthened by the accumulation of contours in the central triangle of metal atoms.

CONCLUSIONS

Since the discovery of the electron in the late 19th century, chemists have speculated about the fate of these particles when they are embedded in molecular matter. The classical theories of Lewis[161] and Langmuir[162,289] have continued to influence reasoning about molecular structure and properties in the century after the advent of quantum mechanics. Molecular-orbital theories have provided a way to connect structure, physical properties, and chemical reactivity on a qualitative level,[4,5,90,290] but quantitative accuracy in *ab initio*, quantum-mechanical calculation persistently demands correlated models of electronic structure. Such requirements appear to undermine the validity of molecular-orbital theory, at least in its *ab initio*, Hartree–Fock realization and to consign Aufbau principles based on delocalized, one-electron functions to quantitative irrelevance. Concepts of chemical bonding that retain their exactitude in the presence of electron interaction therefore constitute a higher standard of credibility in the field of molecular, electronic-structure theory.

Dyson orbitals and their electron binding energies satisfy this standard while retaining many of the conceptual advantages of uncorrelated, molecular-orbital theory. With the advent of incisive spectroscopic techniques and methods of data analysis, it is now possible to infer the complex amplitudes of Dyson orbitals from experimental measurements. Previous generations of spectroscopic and scattering experiments that yielded electron-binding energies also produced data on the squared moduli of Dyson orbitals, which are components of initial-state, electronic densities. Improvements and generalizations of current experimental techniques could, in principle, suffice to reconstruct one-electron-density matrices and total energies. Claims regarding Dyson orbitals that are based on calculations are falsifiable by means of experimental observation. Aufbau principles for the properties of initial, N-electron states are restored to quantitative relevance by the introduction of orbitals and orbital energies that are mapped to final states, each with a spectroscopically meaningful probability factor.

No assumptions regarding traditional, chemical concepts are invoked in this approach to molecular, electronic-structure theory. No model, one-electron Hamiltonians need be introduced. Many-electron *Ansätze* that contain geminal or other group functions never appear. Dyson-orbital concepts are agnostic with respect to the qualitative traditions of molecular-orbital and valence-bond theories, require no neglect of electron interaction, and can be applied universally to any molecular system. There is no formal impediment to calculating Dyson orbitals with many-electron wavefunctions of any provenance.

Dyson orbitals are defined only in terms of many-electron, state functions. Their amplitudes in position or momentum space and their probability factors have a clear physical meaning. Electron densities and reduced-density matrices used to calculate one-electron properties may be constructed from Dyson orbitals. Together with their electron-binding energies, Dyson orbitals are rigorously related to total, electronic energies. Dyson orbitals are eigenfunctions of a well-defined operator that depends only on the density matrices of an initial state. These conclusions follow from the Schrödinger equation with mathematical rigor.

The interpretive apparatus of chemical-bonding theory that is founded on electronic densities or one-electron, reduced-density matrices is readily applicable to Dyson orbitals, which are summable components of both these entities. Dyson orbitals may be analyzed in terms of the real-space or Hilbert-space partitioning schemes that recur in widely used approaches to the recognition of patterns in molecular structure, energetics, spectra, and reactivity. This capability is applicable to molecules in their equilibrium structures or to reacting species in which chemical bonds are forming or breaking. Multi-photon experiments may be interpreted in terms of Dyson orbitals that resemble distinct, localized, hybrid functions that change with time.

Practical calculation of Dyson orbitals need not require the evaluation of many-electron state functions. Direct procedures based on the Dyson quasiparticle equation or the super-operator secular equations provide Dyson orbitals and electron-binding energies with an accuracy that suffices to assign spectra and to provide clear interpretation of chemical bonding in closed-shell and certain kinds of open-shell molecules. Efficient algorithms for performing these calculations continue to be accessible to computational scientists.

Basic chemistry courses that introduce atomic and molecular structure typically present a series of chemical-bonding theories that begins with classical notions such as Lewis's electron dots[161] and octets[162,289] or Gillespie and Nyholm's valence-shell-electron-pair-repulsion model.[153,154] Valence-bond notions[163–166] that invoke quantum-mechanical interference between hybrid orbitals in the formation of bonding pairs often follow. Finally, molecular-orbital theories[291–295] are introduced, but discussion of delocalized orbitals typically is confined to diatomic molecules. At this point, students may be introduced to Dyson orbitals, their electron-binding energies, and probability factors and to the experiments that provide realizations of these concepts.

Exact generalizations that relate uncorrelated, molecular-orbital theory to Dyson-orbital concepts do not abolish the utility of valence-bond or other theories that are founded on group functions or spin couplings that involve two or more electrons. Coincidence experiments of the future that probe two-electron or higher, reduced-density matrices may provide tests of the quality of wavefunctions that incorporate valence-bond or geminal constructs. The experimental relevance, universality, rigor, and computational practicality of one-electron interpretations of electronic structure based on Dyson orbitals do not foreclose advances in the understanding of correlated, many-electron phenomena. Reasoning by analogy can profitably employ terms that explicitly invoke electron correlation. The alternative languages found in chemical-bonding theories will continue to acquire greater flexibility and depth.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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