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Long-range behavior of electronic wave functions. Generalized Carlson-Keller expansion

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The long-range behavior of symmetry-restricted multiconfigurational self-consistent-field orbitals is given by $\chi_{i\alpha a}^{(1)} \sim (k_{i\alpha a} + \mathrm{r}^{-1} A_{i\alpha a})\, r^{\eta_a} e^{-\zeta r}$, where the common orbital exponent ζ comes from the eigenvalue $\zeta^2/2$ of an "ionization potential" matrix $\mathcal{I}^{\bar{\alpha}}$, which may be thought of as being calculated with mixed-symmetry $(N-1)$-electron functions extracted from the N-electron wave function. Here α is a "symmetry" index, a is a "component" index, and i is a "serial" index. The $k_{i\bar{\alpha}a}$ and $A_{i\bar{\alpha}a}$ from the "key" orbitals $\chi_{i\bar{\alpha}a}^{(1)}$ are derived from eigenvectors of $\mathcal{I}^{\bar{\alpha}}$. The corresponding key $\eta_{\bar{\alpha}}$ is obtained from the screened nuclear charge and from ζ by $\eta_{\bar{\alpha}} = (Z - N + 1 - \zeta)/\zeta$, while the other η_a satisfy $\eta_a \le \eta_{\bar{\alpha}} - l_{GT}(\bar{\alpha},\alpha) - 1$, where $l_{GT}(\bar{\alpha},\alpha)$ is the smallest l such that $Y_l^m(\theta,\phi)$ couples $\bar{\alpha}$ to α. The Carlson-Keller "theorem"—the diagonal expansion of the N-electron wave function on its p- and $(N-p)$-electron natural eigenfunctions—is generalized for symmetry-restricted natural eigenfunctions. Distinct symmetry-coupled parts of the wave function can separately but not simultaneously be put in diagonal form.

I. INTRODUCTION

Recently there has been a revival of interest in the long-range behavior of electronic wave functions.[1-13] It is now well established (sometimes even rigorously) that closed-shell Hartree-Fock (HF) orbitals,[1,2] unrestricted natural orbitals,[3,4] ground-state helium natural radial orbitals,[5,6] the exact charge density,[7-9,11,12] and the exact wave function[12,13] are governed by formulas of the form, $r^{\eta} e^{-\zeta r}$, where ζ is related to the ionization potential, and η depends both on ζ and on angular momentum or similar group-theoretical quantum numbers. There is, however, an important class of electronic wave functions not yet asymptotically analyzed—namely, the (symmetry-restricted) multiconfigurational self-consistent-field (MCSCF) wave functions, which are perhaps the most useful currently for *ab initio* calculations. One purpose of this paper is to derive the asymptotic behavior of MCSCF wave functions, which can encompass the Hartree-Fock wave function,[1,2] the exact wave function,[12,13] and those in between.

In their derivation of the asymptotic behavior of unrestricted natural orbitals, Morrell, Parr, and Levy[3] leaned heavily on the Carlson-Keller "theorem,"[14] whose content is the simple internal structure of the wave function when expressed in terms of its p-electron and $(N-p)$-electron natural eigenfunctions. A second purpose of this paper is to generalize the Carlson-Keller theorem to the case that the p-electron and $(N-p)$-electron eigenfunctions are restricted to have correct symmetry properties. The generalized Carlson-Keller theorem does not play so key a derivational role here, but it helps one to understand some of the subtleties.

II. SYMMETRY-RESTRICTED NATURAL ORBITALS AND NATURAL EIGENFUNCTIONS

Although not essential, natural orbitals[15] and natural eigenfunctions[15] facilitate deriving the asymptotic properties of MCSCF orbitals. This section contains an exposition of the properties of symmetry-restricted natural eigenfunctions. The notation and ideas are basic to the next two sections.

Unrestricted natural orbitals[15] (NO) characteristically ignore symmetry. As simple a two-electron wave function as $A(1s2p) + B(3d2p)$ has a mixed-symmetry natural spatial orbital $A(1s) + cB(3d)$. As is apparently well known to practitioners of NO computational procedures for MCSCF wave functions,[16,17] the complication of mixed symmetry is easily avoided by redefining the density matrix to be an average over degenerate wave-function components to make it invariant.

Let G denote the symmetry group of the N-electron Hamiltonian H, and let $\Psi_{\sigma s}$ $(s = 1, 2, \ldots, N_\sigma)$ be degenerate wave functions of H transforming under G according to the N_σ-dimensional irreducible representation $D^{(\sigma)}$ of G. The symmetry-restricted (SR) N-electron density matrix is defined by

$$\Gamma_{\mathrm{SR}}^{(N)}(1,2,\ldots,N;1',2',\ldots,N') = \frac{1}{N_\sigma} \sum_{\sigma=1}^{N_\sigma} \Psi_{\sigma s}(1,2,\ldots,N)\, \Psi_{\sigma s}^{*}(1',2',\ldots,N') . \quad (1)$$

From $\Gamma_{\mathrm{SR}}^{(N)}$, p-electron symmetry-restricted density matrices are found in the usual way by integrating over $N-p$ electrons:

$$\Gamma_{\mathrm{SR}}^{(p)}(1,2,\ldots,p;1',2',\ldots,p')=\binom{N}{p}\int d\tau_{p+1}d\tau_{p+2}\cdots d\tau_N\Gamma_{\mathrm{SR}}^{(N)}(1,2,\ldots,p,p+1,\ldots,N;1',2',\ldots,p',p+1,\ldots,N). \tag{2}$$

$\Gamma_{\mathrm{SR}}^{(N)}$ and consequently all $\Gamma_{\mathrm{SR}}^{(p)}$ are invariant under G. We call their eigenfunctions, which transform irreducibly under G, symmetry-restricted natural eigenfunctions (SRNE) and, in the $p=1$ case, symmetry-restricted natural orbitals (SRNO).

To label p-electron SRNE's, $\chi_{i\alpha a}^{(p)}$, we use three indices: a symmetry-unrelated index i (like principal quantum number), an irreducible representation index α (like "l"), and a component index a (like "m"). The $\Gamma_{\mathrm{SR}}^{(p)}$ have a diagonal expansion on the SRNE's,

$$\Gamma_{\mathrm{SR}}^{(p)}=\sum_i\sum_\alpha n_{i\alpha}^{(p)}\sum_a|\chi_{i\alpha a}^{(p)}\rangle\langle\chi_{i\alpha a}^{(p)}|\,. \tag{3}$$

Note that the occupation numbers $n_{i\alpha}^{(p)}$ do not depend on the component index.

In the $A1s2p+B3d2p$ example above, G is the direct product of the space and spin rotation groups. The SRNO's are $(1s\alpha)$, $(1s\beta)$, $[(2p_m\alpha)$, $(2p_m\beta)$, $m=-1,0,1]$, and $[(3d_m\alpha)$, $(3d_m\beta)$, $m=-2,-1,\ldots,2]$. The corresponding occupation numbers are $n_{1s\alpha}^{(1)}=n_{1s\beta}^{(1)}=\frac{1}{2}A^2$, $n_{2p_m\alpha}^{(1)}=n_{2p_m\beta}^{(1)}=\frac{1}{6}(A^2+B^2)$, and $n_{3d_m\alpha}^{(1)}=n_{3d_m\beta}^{(1)}=\frac{1}{10}B^2$.

In the case of SRNO's, the occupation numbers of α and β spin orbitals are identical. The spatial parts are SR spatial NO*s* whose occupation numbers are twice those of the SRNO's.

Apart from being invariant under G, the $\Gamma_{\mathrm{SR}}^{(p)}$ have the usual normalization and expectation-value properties of non-SR $\Gamma^{(p)}$:

$$\mathrm{Tr}\Gamma_{\mathrm{SR}}^{(p)}=\binom{N}{p}, \tag{4}$$

$$\langle\Psi_{\sigma s}|H|\Psi_{\sigma s}\rangle=\mathrm{Tr}[h(1)\Gamma_{\mathrm{SR}}^{(1)}]+\mathrm{Tr}\left(\frac{1}{r_{12}}\Gamma_{\mathrm{SR}}^{(2)}\right). \tag{5}$$

III. SYMMETRY-RESTRICTED GENERALIZATION OF THE CARLSON-KELLER EXPANSION

The Carlson-Keller expansion[14] is the "diagonal" expansion[18] of Ψ on products of p-electron and $(N-p)$-electron *unrestricted* NE's:

$$\Psi=\sum_i c_i\chi_i^{(p)}(1,2,\ldots,p)\chi_i^{(N-p)}(p+1,p+2,\ldots,N), \tag{6}$$

$$n_i^{(p)}=n_i^{(N-p)}=\binom{N}{p}|c_i|^2. \tag{7}$$

Such a decomposition is in general not possible in the SR case as the following simple, *schematic*, two-electron example shows:

$$\Psi=A(1s2p)+B[3d(2p+3p)]. \tag{8}$$

The s and d SRNO's are $(1s)$ and $(3d)$, but the p SRNO's are neither $(2p)$ nor $(2p+3p)$. Yet these are what appear as co-factors of $(1s)$ and $(3d)$ in Ψ.

This example is more than a counter example; it reveals the nature of the generalization. The (sp) and (pd) contributions to Ψ can *separately* be put into diagonal form, but not necessarily simultaneously, and not necessarily by the SRNO's derived from Ψ.

To reveal more precisely the $p\times(N-p)$ structure of $\Psi_{\sigma s}$, let us analyze its expansion in products of SRNE's. First fix $i\alpha$ and $j\beta$. The $N_\alpha\times N_\beta$ simple products,

$$\chi_{i\alpha a}^{(p)}\chi_{j\beta b}^{(N-p)}=\chi_{i\alpha a}^{(p)}(1,2,\ldots,p)\chi_{j\beta b}^{(N-p)}(p+1,p+2,\ldots,N)$$
$$(a=1,2,\ldots,N_\alpha;\ b=1,2,\ldots,N_\beta), \tag{9}$$

can contribute to $\Psi_{\sigma s}$ only if $D^{(\alpha)}\times D^{(\beta)}$ contains $D^{(\sigma)}$. In that case the linear combination with σs symmetry is completely determined by group theory[19] and normalization:

$$((\chi_{i\alpha}^{(p)}\chi_{j\beta}^{(N-p)}))=\sum_{a=1}^{N_\alpha}\sum_{b=1}^{N_\beta}d_{sab}^{\sigma\alpha\beta}\chi_{i\alpha a}^{(p)}\chi_{j\beta b}^{(N-p)}\,. \tag{10}$$

Here the vector-coupling (Clebsch-Gordan) coefficients have been denoted by $d_{sab}^{\sigma\alpha\beta}$ and normalized by

$$\sum_{a=1}^{N_\alpha}\sum_{b=1}^{N_\beta}|d_{sab}^{\sigma\alpha\beta}|^2=1\,. \tag{11}$$

The $((\chi_{i\alpha}^{(p)}\chi_{j\beta}^{(N-p)}))$ is essentially a "configuration" wave function.

Next let i and j vary. The contribution of all $\alpha\times\beta$ configurations is a sum over i and j:

$$\Psi_{\sigma s}^{[\alpha\beta]}=\sum_i\sum_j c_{i\alpha j\beta}((\chi_{i\alpha}^{(p)}\chi_{j\beta}^{(N-p)})) \tag{12}$$

$$=\sum_i\sum_j c_{i\alpha j\beta}\sum_a^{N_\alpha}\sum_b^{N_\beta}d_{sab}^{\sigma\alpha\beta}\chi_{i\alpha a}^{(p)}\chi_{j\beta b}^{(N-p)}, \tag{13}$$

where the CI coefficients $c_{i\alpha j\beta}$ depend on the configuration label $i\alpha j\beta$, but not on the component labels s,a,b.

Finally, the expansion for $\Psi_{\sigma s}$ is a sum over all couplings $[\alpha\beta]$ that lead to σ:

$$\Psi_{\sigma s}=\sum_\alpha\sum_\beta\Psi_{\sigma s}^{[\alpha\beta]} \tag{14}$$

$$=\sum_\alpha\sum_\beta\sum_i\sum_j c_{i\alpha j\beta}\sum_a^{N_\alpha}\sum_b^{N_\beta}d_{sab}^{\sigma\alpha\beta}\chi_{i\alpha a}^{(p)}\chi_{j\beta b}^{(N-p)}\,. \tag{15}$$

The $c_{i\alpha j\beta}$ are related to the $n_{i\alpha}^{(p)}$ in Eq. (3) via

$n^{(p)}_{i\alpha} = \sum_{\beta j} c^{*}_{\alpha i \beta j} c_{\alpha i \beta j} \binom{N}{p} / N_\alpha$.

Focus now on a single $\Psi^{[\alpha\beta]}_{\sigma s}$. The "unrestricted Carlson-Keller theorem," applied *mutatis mutandis* to Eq. (12), implies that $\Psi^{[\alpha\beta]}_{\sigma s}$ can be put into diagonal form by *its* SRNE's,

$$\Psi^{[\alpha\beta]}_{\sigma s} = \sum_i c^{[\alpha\beta]}_i ((\chi^{(p)[\alpha\beta]}_{i\alpha} \chi^{(N-p)[\alpha\beta]}_{i\beta})) \tag{16}$$

$$= \sum_i c^{[\alpha\beta]}_i \sum_a^{N_\alpha} \sum_b^{N_\beta} d^{\sigma\alpha\beta}_{sab} \chi^{(p)[\alpha\beta]}_{i\alpha a} \chi^{(N-p)[\alpha\beta]}_{i\beta b} \,. \tag{17}$$

The $\chi^{(p)[\alpha\beta]}_{i\alpha a}$ are linear combinations of the $\chi^{(p)}_{i\alpha a}$ (the transformation is independent of the component index a). In general, the $\chi^{(p)[\alpha\beta]}_{i\alpha a}$ will be different for each possible β and from the SRNO's $\chi^{(p)}_{i\alpha a}$. Only if there is a single symmetry β that couples α into σ in the MCSCF wave function will $\chi^{(p)[\alpha\beta]}_{i\alpha a}$ be the same as $\chi^{(p)}_{i\alpha a}$.

In summary, the generalized Carlson-Keller expansion is as follows: an N-electron wave function $\Psi_{\sigma s}$ has the "diagonal" decomposition into products of p- and $(N-p)$-electron functions,

$$\Psi_{\sigma s} = \sum_{\alpha,\beta} \sum_i c^{[\alpha\beta]}_i \sum_a^{N_\alpha} \sum_b^{N_\beta} d^{\sigma\alpha\beta}_{sab} \chi^{(p)[\alpha\beta]}_{i\alpha a} \chi^{(N-p)[\alpha\beta]}_{i\beta b} \,. \tag{18}$$

The $\chi^{(p)[\alpha\beta]}_{i\alpha a}$ and $\chi^{(N-p)[\alpha\beta]}_{i\beta b}$ are SRNE's for the $\alpha \times \beta$ part of $\Psi_{\sigma s}$; in general they are different for each coupling $[\alpha\beta]$ in $\Psi_{\sigma s}$ and from the SRNE's of the full $\Psi_{\sigma s}$. If, however, α appears coupled to only one β, then the $\chi^{(p)[\alpha\beta]}_{i\alpha a}$ and $\chi^{(p)}_{i\alpha a}$ are the same.

IV. ASYMPTOTIC BEHAVIOR OF SYMMETRY-RESTRICTED MCSCF NATURAL ORBITALS

The $r^\eta e^{-\zeta r}$ asymptotic behavior of the SRNO's has three distinct aspects: the form itself, the connection of η to ζ and to the symmetry indices α, and the connection of $\frac{1}{2}\zeta^2$ to an ionization potential *calculated in a basis derived from* $\Psi_{\sigma s}$. The first two are easier to establish than the third, which we can demonstrate directly only for certain MSCSF wave functions. We proceed in three stages: First we set up equations to determine the $\chi^{(1)}_{i\alpha a}$, second we characterize the $r^\eta e^{-\zeta r}$ form, including the specification of η, and third we grapple with the ionization-potential connection—the generalized Koopmans theorem.

A. Equation for SRNO's

The basic equation governing SR-MCSCF orbitals is that $\delta E = 0(|\delta\Psi_{\sigma s}|^2)$ for any variation of the orbitals that preserves the SR-MCSCF form. Suitable variations are unitary transformations (or orthogonal, if realness is a required constraint for the specfic MCSCF wave function), and when applied to $\langle \Psi_{\sigma s} | H | \Psi_{\sigma s} \rangle$ in the density-matrix form of Eq. (5), yield[20,21]

$$\left(h\Gamma^{(1)}_{\text{SR}} + 2\,\text{Tr}^{(2)} \frac{1}{r_{12}} \Gamma^{(2)}_{\text{SR}} \right) \chi^{(1)}_{i\alpha a}$$

$$= \left(\Gamma^{(1)}_{\text{SR}} h + 2\,\text{Tr}^{(2)} \Gamma^{(2)}_{\text{SR}} \frac{1}{r_{12}} \right) \chi^{(1)}_{i\alpha a} \tag{19}$$

$$= \sum_{i'} \lambda^{\alpha}_{ii'} \chi^{(1)}_{i'\alpha a} \,. \tag{20}$$

Here h denotes the one-electron "bare nucleus" operator in the Hamiltonian and $\text{Tr}^{(2)}$ denotes the trace with respect to electron 2. The $\lambda^{\alpha}_{ii'}$ (i and i' have been deliberately transposed) are defined by

$$\lambda^{\alpha}_{ii'} = \left\langle \chi^{(1)}_{i'\alpha a} \middle| \left(\Gamma^{(1)}_{\text{SR}} h + 2\,\text{Tr}^{(2)} \Gamma^{(2)}_{\text{SR}} \frac{1}{r_{12}} \right) \middle| \chi^{(1)}_{i\alpha a} \right\rangle$$

$$(\text{independent of } a) \,. \tag{21}$$

The advantage of the SRNO basis is that $\Gamma^{(1)}_{\text{SR}}$ is diagonal.[22] Note that the operators on the two sides of Eq. (19) are Hermitian conjugates. Thus the $\lambda^{\alpha}_{ii'}$ form Hermitian matrices[23] λ^α.

B. Asymptotic form of SRNO's: $\chi^{(1)}_{i\alpha a} \sim k_{i\alpha a} r^{\eta_\alpha} e^{-\zeta r}$

Equation (20) resembles the *noncanonical* Hartree-Fock equation. The reasoning[1,2] used in the Hartree-Fock case can be applied to find the asymptotic form of the $\chi^{(1)}_{i\alpha a}$.

The operator $2\,\text{Tr}^{(2)}[(1/r_{12})\Gamma^{(2)}_{\text{SR}}]$ on the left-hand side of Eq. (20) plays the role of the Coulomb and exchange operators in Hartree-Fock theory. The operator decomposes asymptotically into a screening term and into r-dependent, symmetry-coupling, scrambling terms via Laplace's expansion for $1/r_{12}$:

$$2\,\text{Tr}^{(2)} \frac{1}{r_{12}} \Gamma^{(2)}_{\text{SR}} \chi^{(1)}_{i\alpha a} \sim \frac{N-1}{r_1} \Gamma^{(1)}_{\text{SR}} \chi^{(1)}_{i\alpha a}$$

$$+ \sum_{l=1}^{\infty} \sum_{mj\beta b} \Lambda^{lm}_{j\beta b,\, i\alpha a} r_1^{-l-1} Y^m_l \chi^{(1)}_{j\beta b} \,,$$

$$\text{as } r_1 \to \infty \,, \tag{22}$$

where

$$\Lambda^{lm}_{j\beta b,\, i\alpha a} \equiv \frac{4\pi}{2l+1} \langle \chi^{(1)}_{j\beta b} | \, 2\,\text{Tr}^{(2)} r_2^l Y^m_l(\theta_2, \phi_2)^* \Gamma^{(2)}_{\text{SR}} \, | \chi^{(1)}_{i\alpha a} \rangle \,. \tag{23}$$

With Eq. (22), and with $h \sim -\frac{1}{2} d^2/dr^2 - (1/r) d/dr - Z/r + O(r^{-2})$, where Z is the total nuclear charge of the atom or molecule, Eq. (20) at large r takes the form

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} \frac{d}{dr} - \frac{Z-N+1}{r} + O(r^{-2}) \right) n^{(1)}_{i\alpha} \chi^{(1)}_{i\alpha a}$$

$$+ \sum_{l=1}^{\infty} \sum_{mj\beta b} \Lambda^{lm}_{j\beta b,\, i\alpha a} r^{-l-1} Y^m_l \chi^{(1)}_{j\beta b} \sim \sum_{i'} \lambda^{\alpha}_{ii'} \chi^{(1)}_{i'\alpha a} \,. \tag{24}$$

We anticipate[1-13] asymptotic solutions of Eq. (24) with the form

$$\chi_{i\alpha a}^{(1)} \sim (k_{i\alpha a}+A_{i\alpha a}r^{-1})r^{\eta_{i\alpha}}e^{-\zeta r}\,, \tag{25}$$

where the $k_{i\alpha a}$, $A_{i\alpha a}$, $\eta_{i\alpha}$, and ζ have values yet to be found. [The $k_{i\alpha a}$ and $A_{i\alpha a}$ are functions of angle; in atoms they would be proportional to $Y_l^m(\theta,\phi)$.] There is a common exponential[1-13] factor $e^{-\zeta r}$ because of the Λ terms in Eq. (24).

Because the $\chi_{i\alpha a}^{(1)}$ for fixed αa are scrambled by λ^α in Eq. (24), it is reasonable to assume that $\eta_{i\alpha}$ is independent of i: $\eta_{i\alpha}=\eta_\alpha$. Examples of dependence on i occur already at the Hartree-Fock level,[2] but these are really special cases where the $n_{i\alpha}^{(1)}$ and λ^α have special values. Without knowledge of the values of λ^α and the $n_{i\alpha}^{(1)}$, one cannot obtain i dependence from Eq. (24). (See Sec. IV D for a few special cases.) For the ground state of helium, which is not a special case, no i dependence seems to be found[5,6-13] for the η_α numerically.

Towards evaluating ζ, $k_{i\alpha a}$, etc., we put into Eq. (24) the asymptotic formula (25) (with η_α for $\eta_{i\alpha}$) to obtain the asymptotic equation

$$n_{i\alpha}^{(1)}\{-\tfrac{1}{2}\zeta^2k_{i\alpha a}+r^{-1}[(\zeta\eta_\alpha+\zeta-Z+N-1)k_{i\alpha a}-\tfrac{1}{2}\zeta^2A_{i\alpha a}]+O(r^{-2})\}r^{\eta_\alpha}e^{-\zeta r}$$
$$+\sum_{l=1}^{\infty}\sum_{mj\beta b}\Lambda_{j\beta b,i\alpha a}^{lm}Y_l^m(\theta,\phi)[k_{j\beta b}+O(r^{-1})]r^{\eta_\beta-l-1}e^{-\zeta r}=\sum_{i'}\lambda_{ii'}^{\alpha}[k_{i'\alpha a}+r^{-1}A_{i'\alpha a}+O(r^{-2})]r^{\eta_\alpha}e^{-\zeta r}\,. \tag{26}$$

Focus first on the maximum η_α, say $\eta_{\bar\alpha}$, taken on for $\alpha=\bar\alpha$. (There can be more than one $\bar\alpha$ with the same maximum $\eta_{\bar\alpha}$.) Since the Λ terms are $O(r^{\eta_{\bar\alpha}-l-1}e^{-\zeta r})$ $(l\geqslant 1)$, equality of the $r^{\eta_{\bar\alpha}}e^{-\zeta r}$—terms in Eq. (26) yields generalized eigenvalue equations that determine both ζ and the $k_{i\bar\alpha a}$:

$$-\tfrac{1}{2}\zeta^2 n_{i\bar\alpha}^{(1)}k_{i\bar\alpha a}=\sum_{i'}\lambda_{ii'}^{\bar\alpha}k_{i'\bar\alpha a}\,. \tag{27}$$

Equation (27) can be set as a simpler ordinary eigenvalue problem by incorporating $(n_{i\bar\alpha}^{(1)})^{-1}$ into the operator $\lambda^{\bar\alpha}$:

$$g_{ii'}^{\alpha}\equiv-(n_{i\alpha}^{(1)})^{-1/2}\lambda_{ii'}^{\alpha}(n_{i'\alpha}^{(1)})^{-1/2}\,, \tag{28}$$

$$\sum_{i'}g_{ii'}^{\bar\alpha}[(n_{i'\bar\alpha}^{(1)})^{1/2}k_{i'\bar\alpha a}]=\tfrac{1}{2}\zeta^2[(n_{i\bar\alpha}^{(1)})^{1/2}k_{i\bar\alpha a}]\,. \tag{29}$$

Thus the $N_{\bar\alpha}$ vectors

$$\{[(n_{1\bar\alpha}^{(1)})^{1/2}k_{1\bar\alpha a},(n_{2\bar\alpha}^{(1)})^{1/2}k_{2\bar\alpha a},\ldots]\,|\,a=1,2,\ldots,N_{\bar\alpha}\}$$

are (irreducibly transforming) eigenvectors of $g^{\bar\alpha}$ with eigenvalue $\frac{1}{2}\zeta^2$.

Focus next on the $r^{\eta_{\bar\alpha}-1}e^{-\zeta r}$—terms in Eq. (26). Use the adjoint of Eq. (27) to evaluate the scalar product of $(k_{1\bar\alpha a},k_{2\bar\alpha a},\ldots)^*$ with Eq. (26) and obtain two results. First,

$$\eta_{\bar\alpha}=(Z-N+1-\zeta)/\zeta\,, \tag{30}$$

and second, $[(n_{1\bar\alpha}^{(1)})^{1/2}A_{1\bar\alpha a},(n_{2\bar\alpha}^{(1)})^{1/2}A_{2\bar\alpha a},\ldots]$ is also an (irreducibly transforming) eigenvector of $g^{\bar\alpha}$ with eigenvalue $\frac{1}{2}\zeta^2$. Unless there is accidental degeneracy, the $A_{i\bar\alpha a}$ are necessarily proportional to the $k_{i\bar\alpha a}$.

We now determine in two steps the η_α that are less than $\eta_{\bar\alpha}$. The first step is to show that

$$\eta_\alpha=\max[\eta_\beta-l_{\min}(\beta,\alpha)-1]\,, \tag{31}$$

where $l_{\min}(\beta,\alpha)$ is the smallest l for which some $\Lambda_{j\beta b,i\alpha a}^{lm}$ is nonzero. The proof is to compare the r^{η_α} and $r^{\eta_\beta-l-1}$ terms in Eq. (26). If $\eta_\alpha>\eta_\beta-l_{\min}(\beta,\alpha)-1$ for all β, then the Λ terms are ignorable, and we are led as before to $\eta_\alpha=\eta_{\bar\alpha}$. If $\eta_\alpha<\eta_\beta-l_{\min}(\beta,\alpha)-1$ for some β, then the r^{η_α} terms would be ignorable, and a sum of Λ terms would have to vanish, which except in special cases[24] seems unlikely. Thus $\eta_\alpha=\max[\eta_\beta-l_{\min}(\beta,\alpha)-1]$.

Let η_{α_1} be the next largest after $\eta_{\bar\alpha}$. Equation (31) implies

$$\eta_{\alpha_1}=\eta_{\bar\alpha}-l_{\min}(\bar\alpha,\alpha_1)-1\,. \tag{32}$$

Let η_{α_2} be the third largest. Then

$$\eta_{\alpha_2}=\max[\eta_{\bar\alpha}-l_{\min}(\bar\alpha,\alpha_2)-1,\ \eta_{\alpha_1}-l_{\min}(\alpha_1,\alpha_2)-1] \tag{33}$$

$$=\max[\eta_{\bar\alpha}-l_{\min}(\bar\alpha,\alpha_2)-1,\ \eta_{\bar\alpha}-l_{\min}(\bar\alpha,\alpha_1)-l_{\min}(\alpha_1,\alpha_2)-2]\,, \tag{34}$$

and so forth. The second step is to estimate the right-hand sides of Eqs. (31)–(34) by a group-theoretical selection rule: $\Lambda_{j\beta b,i\alpha a}^{lm}$ can be nonzero only if $D^{(l)}\times D^{(\beta)}$ contains $D^{(\alpha)}$.

Let $l_{GT}(\beta,\alpha)$ be the smallest nonzero such l [nonzero, because $l\geqslant 1$ in Eq. (26)]. Note that $l_{GT}(\beta,\alpha)\leqslant l_{\min}(\beta,\alpha)$, since $\Lambda_{j\beta a,i\alpha a}^{lm}$ can still vanish, even though permitted not to. The crucial simplification brought about by the l_{GT} comes from the triangle inequality, $l_{GT}(\bar\alpha,\beta)+l_{GT}(\beta,\alpha)\geqslant l_{GT}(\bar\alpha,\alpha)$, which is a consequence of G's being a subgroup of the full three-dimensional rotation group. Accordingly, Eqs. (31)–(34) become

$$\eta_{\alpha} \leqslant \eta_{\bar{\alpha}} - l_{GT}(\bar{\alpha}, \alpha) - 1 \,. \tag{35}$$

For the ground state of helium, $\bar{\alpha}$ refers to s orbitals, α to $p, d, \ldots$. There is no difference between l_{GT} and $l_{\min}$, and (35) as an equality is verified by numerical calculations.[5,6,13]

To recapitulate, solutions of the asymptotic SRNO equation (24) have the form $\chi^{(1)}_{i\alpha a} \sim (k_{i\alpha a} + r^{-1}A_{i\alpha a}) r^{\eta_\alpha} e^{-\zeta r}$, where $\frac{1}{2}\zeta^2$ is an eigenvalue of $\mathscr{g}^{\bar{\alpha}}$ [Eqs. (28), (29), (19), and (20)], where $(n^{(1)}_{i\bar{\alpha}a})^{1/2} k_{i\bar{\alpha}a}$ and $(n^{(1)}_{i\bar{\alpha}a})^{1/2} A_{i\bar{\alpha}a}$ are the elements of irreducibly transforming eigenvectors of $\mathscr{g}^{\bar{\alpha}}$, where $\eta_{\bar{\alpha}} = (Z - N + 1 - \zeta)/\zeta$, and where the other η_{α} are "keyed" from $\eta_{\bar{\alpha}}$ by Eq. (35). For each eigenvalue of each $\mathscr{g}^{\alpha}$ there will be such a solution. All might be present in each $\chi^{(1)}_{j\beta b}$ at moderate r, but the asymptotic solution with smallest ζ present will dominate at large r.

C. Connection of $\frac{1}{2}\zeta^2$ with the ionization potential

Morrell, Parr, and Levy[3] were the first to obtain the general result, that for unrestricted NOs, $\frac{1}{2}\zeta^2$ is the ionization potential *calculated in the basis of the* $(N-1)$*-electron unrestricted NEs*, $\{\chi^{(N-1)}_i\}$. Katriel and Davidson[13] obtained a consistent, partially stronger result, that $\frac{1}{2}\zeta^2$ should be the exact ionization potential (implying that, for the ionized state, the $\chi^{(N-1)}_i$ are complete). Both results are subject to the criticism raised by Ahlrichs[8] regarding interchanging double-limit processes. The derivation for the SRNO case given here borrows from these earlier treatments.[2,3,5,13]

1. When $\Psi_{\sigma s}$ is the exact wave function

The problem is how to connect $\mathscr{g}^{\alpha}$ [Eq. (28)] with the $(N-1)$-electron Hamiltonian, $H^{(N-1)}$. If for the moment we assume that $\Psi_{\sigma s}$ is the exact wave function, then $\langle \delta\Psi_{\sigma s} | H - E | \Psi_{\sigma s} \rangle = 0$ for any $\delta\Psi_{\sigma s}$. The connection then follows from generating $\delta\Psi_{\sigma s}$ by

$$\delta\chi^{(1)}_{i\alpha a} = \epsilon \chi^{(1)}_{i'\alpha a} \quad (a = 1, 2, \ldots, N_{\alpha}) \,. \tag{36}$$

The detailed decomposition of the $H - E$ matrix element is lengthy. Use Eq. (15) for $\Psi_{\sigma s}$. Put only electron 1 (not electrons $2, \ldots, N$) in $\delta\chi^{(1)}_{i\alpha a}$, and multiply the matrix element by N. Separate from H all the terms not involving electron 1: $[H^{(N-1)}(2, 3, \ldots, N)]$. Use the definition of $\Gamma^{(1)}_{\mathrm{SR}}$ and $\Gamma^{(2)}_{\mathrm{SR}}$ [Eq. (2)] with terms from H involving electron 1. Use the invariance under G of $\Gamma^{(1)}_{\mathrm{SR}}$, $\Gamma^{(2)}_{\mathrm{SR}}$, and $H^{(N-1)}$ to eliminate symmetry-forbidden matrix-element factors, and use the normalization (11) of the $d^{\sigma\alpha\beta}_{sab}$ in the evaluating the remaining $H^{(N-1)}$ contributions. Obtain accordingly [$\delta\Psi_{\sigma s}$("36") represents the $\delta\Psi_{\sigma s}$ generated by Eq. (36)],

$$O = \frac{1}{N_\sigma} \sum_s \langle \delta\Psi_{\sigma s}(\text{"36"}) \,|\, (H - E) \,|\, \Psi_{\sigma s} \rangle \tag{37}$$

$$= \frac{1}{N_\sigma} \sum_s \sum_{j\beta} c^{*}_{i\alpha j\beta} \sum_{ab} d^{\sigma\alpha\beta *}_{sab} N \left\langle (\delta\chi^{(1)}_{i\alpha a}) \chi^{(N-1)}_{j\beta b} \right| \left(h(1) + \sum_{k=2}^{N} \frac{1}{r_{1k}} + H^{(N-1)} - E \right) \left| \Psi_{\sigma s} \right\rangle \tag{38}$$

$$\begin{aligned} &= \sum_a \left\langle \delta\chi^{(1)}_{i\alpha a} \right| \left(h\Gamma^{(1)}_{\mathrm{SR}} + 2\,\mathrm{Tr}^{(2)} \frac{1}{r_{12}} \Gamma^{(2)}_{\mathrm{SR}} \right) \left| \chi^{(1)}_{i\alpha a} \right\rangle \\ &\quad + \sum_{jj'\beta} \sum_{i''} N c^{*}_{i\alpha j\beta} c_{i''\alpha j'\beta} \langle \delta\chi^{(1)}_{i\alpha a'} | \chi^{(1)}_{i''\alpha a'} \rangle \langle \chi^{(N-1)}_{j\beta b'} \,|\, (H^{(N-1)} - E) \,|\, \chi^{(N-1)}_{j'\beta b'} \rangle, \quad (\text{any } a', \text{ any } b') \end{aligned} \tag{39}$$

$$= \epsilon^{*} N_{\alpha} \left[\left\langle \chi^{(1)}_{i'\alpha a} \right| \left(h\Gamma^{(1)}_{\mathrm{SR}} + \mathrm{Tr}^{(2)} \frac{1}{r_{12}} \Gamma^{(2)}_{\mathrm{SR}} \right| \left. \chi^{(1)}_{i\alpha a} \right\rangle + \sum_{jj'\beta b} N N_{\alpha}^{-1} N_{\beta}^{-1} c^{*}_{i\alpha j\beta} c_{i'\alpha j'\beta} \langle \chi^{(N-1)}_{j\beta b} \,|\, (H^{(N-1)} - E) \,|\, \chi^{(N-1)}_{j'\beta b} \rangle \right] (\text{any } a) \,. \tag{40}$$

Then compare Eq. (40) with Eqs. (19)–(21) and (28) to obtain

$$\mathscr{g}^{\alpha}_{ii'} = \frac{1}{N_\beta} \sum_{jj'\beta b} \left(\frac{N}{N_{\alpha} n^{(1)}_{i\alpha}} \right)^{1/2} c^{*}_{i\alpha j\beta} \langle \chi^{(N-1)}_{j\beta b} \,|\, (H^{(N-1)} - E) \,|\, \chi^{(N-1)}_{j'\beta b} \rangle c_{i'\alpha j'\beta} \left(\frac{N}{N_{\alpha} n^{(1)}_{i'\alpha}} \right)^{1/2} . \tag{41}$$

$\mathscr{g}^{\alpha}_{ii'}$ is beginning to look like a matrix element of $H^{(N-1)} - E$. By defining somewhat contrived $(N-1)$-electron functions $\Phi^{(N-1)}_{i\alpha}$, which are of mixed symmetry even though they arise in a SR setting, the resemblance can be made complete:

$$\Phi^{(N-1)}_{i\alpha} \equiv N^{1/2} N_{\alpha}^{-1/2} (n^{(1)}_{i\alpha})^{-1/2} \sum_{j\beta} c_{i\alpha j\beta} N_{\beta}^{-1/2} \sum_{b} \chi^{(N-1)}_{j\beta b} \,, \tag{42}$$

$$\mathscr{g}^{\alpha}_{ii'} = \langle \Phi^{(N-1)}_{i\alpha} \,|\, (H^{(N-1)} - E) \,|\, \Phi^{(N-1)}_{i'\alpha} \rangle \,. \tag{43}$$

For different α, α', the $\Phi^{(N-1)}_{i\alpha}$ do not have to be orthogonal. For the same α, they are related to $\Gamma^{(1)}_{\mathrm{SR}}$ and are orthonormal:

$$\langle \Phi^{(N-1)}_{i\alpha} \,|\, \Phi^{(N-1)}_{i'\alpha} \rangle = N N_{\alpha}^{-1} (n^{(1)}_{i\alpha} n^{(1)}_{i'\alpha})^{-1/2} \sum_{j\beta} c^{*}_{i\alpha j\beta} c_{i'\alpha j\beta} \tag{44}$$

$$= \delta_{ii'} \,. \tag{45}$$

The $\Phi_{i\alpha}^{(N-1)}$ here play the same role as the unrestricted NEs in Ref. 3. Clearly, the eigenvalues of $\mathcal{I}^{\alpha}$ are ionization potentials, the accuracy of which depend only on the ability of the $\Phi_{i\alpha}^{(N-1)}$ to represent eigenfunctions of $H^{(N-1)}$.

2. *When $\Psi_{\sigma s}$ is not the exact wave function*

The initial equations in the preceding derivation, Eqs. (36) and (37), are not universally applicable to SR-MCSCF wave functions. At the least, Eq. (36) must be supplemented by the reciprocal, orthogonality-maintaining change in $\chi_{i'\alpha a}^{(1)}$,

$$\delta\chi_{i'\alpha a}^{(1)} = -\epsilon^{*}\chi_{i\alpha a}^{(1)} . \tag{46}$$

If, however, Eq. (46) were superfluous, then the derivation would hold.

Note that Eqs. (37)–(40) are all proportional to ϵ^*. Equation (46) introduces an analogous set of terms proportional to ϵ. If ϵ can be complex, replacement of ϵ by $i\epsilon$ shows that the ϵ^* and ϵ terms must separately vanish, and the derivation leading to Eq. (43) for $\mathcal{I}_{ii'}^{\alpha}$ is valid. The usual Hartree-Fock[25] and the complete MCSCF generated by a fixed number of orbitals are thus included.

There are, however, MCSCF wave functions for which ϵ is necessarily restricted to be real. A simple example is the two-configuration wave function,

$$A1s^22p^2 + B2s^23p^2 . \tag{47}$$

The variation

$$(1s \to 1s + i|\epsilon|2s,\ \ 2s \to 2s + i|\epsilon|1s)$$

leads to complex s orbitals, which are usually not permitted in a practical calculation. Another way of viewing the same example is that $(1s2s)(A2p^2 - B3p^2)$ cannot mix directly with the real-valued MCSCF function (44) at self-consistency, but $(1s2s)(A2p^2 + B3p^2)$ can. Thus the derivation demonstrates equality of $\mathcal{I}_{ii'}^{\alpha}$ with $H^{(N-1)} - E$ matrix elements only for certain, although rather general, MCSCF wave functions, for which complex variation is permitted.

Even for those MCSCF cases in which $\mathcal{I}_{ii'}^{\alpha}$ is not an explicit matrix element of $H^{(N-1)} - E$, one can regard $\mathcal{I}_{ii'}^{\alpha}$ as an approximation to the corresponding matrix element connected with the exact wave function. In this looser sense, the eigenvalues of $\mathcal{I}^{\alpha}$ may always be regarded as approximate ionization potentials.

D. Special cases with stronger results

The specific nature of the MCSCF wave function or of the symmetry (σs) of the state $\Psi_{\sigma s}$ sometimes permits stronger conclusions than Eq. (35) regarding the prefactors r^{η}. Three such examples are given here.

1. *Closed-shell Hartree-Fock*

The canonical closed-shell Hartree-Fock equations have $\mathcal{I}_{ii'}^{\alpha} = \lambda_{ii'}^{\alpha} = \epsilon_{i\alpha}\delta_{ii'}$. The right-hand side of Eq. (20) does not scramble canonical Hartree-Fock orbitals, and so orbitals of symmetry $\bar{\alpha}$ can have different $\eta_{i\bar{\alpha}}$. See Ref. 2 for the details.

A more specialized case[24] is an atomic Hartree-Fock state involving only s orbitals: e.g., $1s^22s^2$ Be. The "exchange" terms in Eq. (22) are exponentially small at large r, and each orbital has its own ζ. See Ref. 1.

2. *$1s^2$ He*

The ^1S nature of the helium ground state makes the generalized Carlson-Keller expansion reduce to a special case of the unrestricted expansion. The $\chi_{i\alpha a}^{(1)}$ are just of the form $R_{il}(r)Y_l^m(\theta,\phi) \times$ (spin function), and the $(N-1)$-electron $\chi_{i\alpha a}^{(N-1)}$ constitute the same set of SRNO's. The $\Phi_{i\alpha}^{(1)}$ can be redefined to be the $\chi_{i\alpha a}^{(N-1)}$. See Refs. 5 and 6 for details, and also Ref. 13 for related remarks.

3. *"Accidentally degenerate" SRNO's*

If two occupation numbers for the same symmetry are identical, $n_{i\alpha}^{(1)} = n_{i'\alpha}^{(1)}$, then it is possible to have chosen[22] the $\chi_{i\alpha a}^{(1)}$ and $\chi_{i'\alpha a}^{(1)}$ so that one, say i', vanishes more strongly—that is, so that $\eta_{i'\alpha} < \eta_{i\alpha}$. The Hartree-Fock case is again a simple example.[2]

E. On the eigenfunctions of the ionization potential matrices $\mathcal{I}^{\alpha}$

If the $\Phi_{i\alpha}^{(N-1)}$ were complete, then the eigenvalues of $\mathcal{I}^{\alpha}$ would be exactly ionization potentials. When the $\Phi_{i\alpha}^{(N-1)}$ are of mixed symmetry, the implication is that the wrong-symmetry components would have to drop out. Consider as an example the $1s2p\,^1P$ state of helium, whose wave function has the form,

$$\Psi = \sum_{ij} c_{ji}^{sp}((\chi_{js}^{(1)}\chi_{ip}^{(1)})) + \sum_{ij} c_{ij}^{pd}((\chi_{ip}^{(1)}\chi_{jd}^{(1)})) + \cdots . \tag{48}$$

The dominant ζ should correspond to the ionized state $1s$ He$^+$, which would have the smallest eigenvalue of $\mathcal{I}^{p}$. The $\Phi_{ip}^{(1)}$ are mixtures of s and d: *schematically*,

$$\Phi_{ip}^{(1)} = \left(\frac{2}{n_{ip}^{(1)}}\right)^{1/2}\left(\sum_j c_{ji}^{sp}\chi_{js}^{(1)} + \sum_j c_{ij}^{pd}\chi_{jd}^{(1)}\right) . \tag{49}$$

The lowest eigenfunction of $H^{(N-1)}$ is e^{-2r}, so one would expect the expansion on the Φ_{ip} to yield (where A is a proportionality constant),

$$Ae^{-2r}=2^{-1/2}\sum_i (n_{ip}^{(1)})^{1/2}k_{ip}\Phi_{ip}^{(1)} \tag{50}$$

$$=\left(\sum_{i,j}k_{ip}c_{ji}^{sp}\chi_{js}^{(1)}+\sum_{i,j}k_{ip}c_{ij}^{sd}\chi_{jd}^{(1)}\right). \tag{51}$$

Thus one predicts

$$\sum_i k_{ip}c_{ji}^{sp}=A\langle\chi_{js}^{(1)}|e^{-2r}\rangle, \tag{52}$$

$$\sum_i k_{ip}c_{ij}^{sd}=0. \tag{53}$$

If the $\chi_{ip}^{(1)}$ are taken not as the SRNO's of the full Ψ, but as the SRNO's of the *sp* component, then c_{ji}^{sp} would be diagonal, and $k_{ip}c_i^{[sp]}=A\langle\chi_{is}^{(1)}|e^{-2r}\rangle$. A similar prediction[5] for the $1s^2\,{}^1S$ He was verified by Katriel and Davidson.[13] The interesting difference here is the additional orthogonality result (53). (Cf. also Ref. 12.)

For finite MCSCF, the Eqs. (50)–(53) do not necessarily hold exactly, only approximately. In particular, it would appear that the lowest eigenfunction of finite $\mathscr{g}^p$ will have some *d* character.

F. Connection with Katriel and Davidson's analysis of the exact wave function

In a recent paper Katriel and Davidson[13] analyzed the exact $\Psi_{\sigma s}$ in terms of products of exact $(N-1)$-electron wave functions $\psi_j^{(N-1)}(2,3,\ldots,N)$ and their cofactors $f_j(1)$: $\Psi_{\sigma s}=\sum_j f_j\psi_j^{(N-1)}$. We examine their decomposition from the SR-MCSCF point of view.

We exploit the property that the eigenvectors of $\mathscr{g}^\alpha$ approximate eigenfunctions of $H^{(N-1)}$. Let U^α be the unitary matrix whose columns are eigenvectors of $\mathscr{g}^\alpha$. Let the first column of $U^{\bar\alpha}$ be the eigenvector associated with the dominant orbital exponent ζ. That is,

$$U_{i1}^{\bar\alpha}=A(n_{i\bar\alpha}^{(1)})^{1/2}k_{i\alpha}\quad(i=1,2\ldots), \tag{54}$$

where A is a normalization constant. The U^α induce a further decomposition of $\Psi_{\sigma s}$ from the form of Eq. (15):

$$\Psi_{\sigma s}=\sum_{i\alpha a}\left[\sum_{i'}(U^{\alpha\dagger})_{ii'}\left(\frac{n_{i'\alpha}^{(1)}}{N}\right)^{1/2}\chi_{i'\alpha a}^{(1)}\right]\times\left[\sum_{i''}\sum_{j\beta b}\left(\frac{N}{n_{i''\alpha}^{(1)}}\right)^{1/2}U_{i''i}^{\alpha}c_{i''\alpha j\beta}d_{sab}^{\sigma\alpha\beta}\chi_{j\beta b}^{(N-1)}\right] \tag{55}$$

[only the unitarity of the U^α has been used in Eq. (55)]. The functions,

$$\psi_{[i''\alpha a]}^{(N-1)}=\sum_{i''}\sum_{j\beta b}\left(\frac{N}{n_{i''\alpha}^{(1)}}\right)^{1/2}U_{i''i}^{\alpha}c_{i''\alpha j\beta}d_{sab}^{\sigma\alpha\beta}\chi_{j\beta b}^{(N-1)}, \tag{56}$$

are approximate eigenfunctions of $H^{(N-1)}$ in the sense that [cf. Eqs. (41)–(45)],

$$N_\alpha^{-1}\sum_q\left\langle\psi_{[i'''\alpha a]}^{(N-1)}\middle|(H^{(N-1)}-E)\middle|\psi_{[i\alpha a]}^{(N-1)}\right\rangle=(U^{\alpha\dagger}\mathscr{g}^\alpha U^\alpha)_{i'''i}. \tag{57}$$

This decomposition is almost that of Katriel and Davidson. The difference is that there the terms with the same $(N-1)$-electron wave function are grouped together. We cannot quite group such terms here because $\psi_{[i\alpha a]}^{(N-1)}$ and $\psi_{[i'\alpha' a']}^{(N-1)}$ may be nonidentical approximations to the same $(N-1)$-electron state, arising from different $\mathscr{g}^\alpha$ and $\mathscr{g}^{\alpha'}$.

Now focus on the $\mathscr{g}^{\bar\alpha}$ that produces the dominant ζ. The function holding electron 1 in Eq. (55) which is the cofactor of $\psi_{[i\bar\alpha a]}^{(N-1)}$ is

$$f_{i\bar\alpha a}^{(1)}=\sum_{i'}(U^{\bar\alpha\dagger})_{ii'}\left(\frac{n_{i'\bar\alpha}^{(1)}}{N}\right)^{1/2}\chi_{i'\bar\alpha a}^{(1)}. \tag{58}$$

We examine $f_{i\bar\alpha a}^{(1)}$ asymptotically, via Eqs. (25) and (54):

$$f_{i\bar\alpha a}^{(1)}=\sum_{i'}(U^{\bar\alpha\dagger})_{ii'}\left(\frac{n_{i'\bar\alpha}^{(1)}}{N}\right)^{1/2}[k_{i'\bar\alpha a}+r^{-1}A_{i'\bar\alpha a}+O(r^{-2})]r^{\eta_{\bar\alpha}}e^{-\zeta r} \tag{59}$$

$$=\sum_{i'}(U^{\bar\alpha\dagger})_{ii'}N^{-1/2}[A^{-1}U_{i'1}^{\bar\alpha}(1+r^{-1}B)+O(r^{-2})]r^{\eta_{\bar\alpha}}e^{-\zeta r} \tag{60}$$

$$=\delta_{i1}N^{-1/2}A^{-1}(1+r^{-1}B)r^{\eta_{\bar\alpha}}e^{-\zeta r}+O(r^{\eta_{\bar\alpha}-2}e^{-\zeta r}). \tag{61}$$

(B is a proportionality factor.) Thus the one-electron cofactor of the dominant $(N-1)$-electron state $(i=1)$ goes asymptotically like $r^{\eta_{\bar\alpha}}e^{-\zeta r}$; all other cofactors with the same symmetry $\bar\alpha$ $(i\neq 1)$ vanish more strongly. This is essentially the result of Katriel and Davidson,[13] carried over to SRNO's.

V. SUMMARY

Two aspects of the structure of electronic wave functions have been discussed. (i) The expansion of an N-electron wave function on products of p-electron and $(N-p)$-electron symmetry-restricted natural eigenfunctions is not in general diagonal, but each distinct symmetry-coupled part can be separately put in diagonal form (generalized Carlson-Keller expansion, Sec. III). (ii) The asymptotic behavior of symmetry-restricted natural orbitals of finite MCSCF wave functions $\Psi_{\sigma s}$ is given by $\chi_{i\alpha a}^{(1)}\sim(k_{i\alpha a}+r^{-1}A_{i\alpha a})r^{\eta_\alpha}e^{-\zeta r}$, where $\frac{1}{2}\zeta^2$ is the eigenvalue of an "ionization-potential" matrix $\mathscr{g}^{\bar\alpha}$. For complex-variation stable MCSCF, $\mathscr{g}^{\bar\alpha}$ is calculated from $H^{(N-1)}-E$ via $(N-1)$-electron basis functions extracted from $\Psi_{\sigma s}$. For the key symmetry $\bar{\alpha}$, the $k_{i\bar{\alpha}a}$ and $A_{i\bar{\alpha}a}$ are related to eigenvectors of $\mathcal{G}^{\bar{\alpha}}$, and $\eta_{\bar{\alpha}}$ is given by $(Z-N+1-\zeta)/\zeta$. The other η_α satisfy $\eta_\alpha \leqslant \eta_{\bar{\alpha}} - l_{GT}(\bar{\alpha}, \alpha) - 1$, where $l_{GT}(\bar{\alpha}, \alpha)$ is the smallest l for which Y_l^m couple α to $\bar{\alpha}$. The most general results apply rigorously to finite MCSCF wave functions that are stationary to unitary transformation of the orbital shells. It is reasonable that they apply also to the exact wave function, but then one would have to justify[8] interchanging the two limits: $r \to \infty$, number of configurations $\to \infty$. For some special cases, simpler, stronger results can be obtained in which the $\eta_{i\alpha}$ depend on i; the closed-shell Hartree-Fock case is such an example.

The asymptotic properties of SRNO's are consistent with the results of Katriel and Davidson[13] for the cofactors of exact $(N-1)$-electron wave functions imbedded in $\Psi_{\sigma s}$.

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[17] Cf. W. Kutzelnigg, Z. Naturforschg. 18a, 1058 (1963); R. McWeeny and W. Kutzelnigg, Int. J. Quantum Chem. 2, 187 (1968).

[18] Here "diagonal" is used somewhat loosely. When $p=N-p$, the $\chi_i^{(p)}$ and $\chi_i^{(N-p)}$ can be different functions, as in the diagonal two-electron wave function, $A1s2p + B2s3p + C3s4p$. The precise meaning is that each $\chi_i^{(p)}(1, \ldots, p)$ [and each $\chi_j^{(N-p)}(p+1, \ldots, N)$] can appear in only one term in the expansion.

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[22] Note that Eq. (19) is homogeneous in the $\chi_{i\alpha a}^{(1)}$. The system of equations is therefore valid for any unitary transformation of the SRMCSCF orbitals.

[23] Hermiticity is only guaranteed for the converged MCSCF solution, and not necessarily for unconverged iterative approximations.

[24] If, for a fixed α, *all* $\Lambda_{j\beta b, i\alpha a}^{lm}$ are zero, then the $\chi_{i\alpha a}^{(1)}$ are not exchange coupled to other $\chi_{j\beta b}^{(1)}$, and the $\chi_{i\alpha a}^{(1)}$, have their own orbital exponent, ζ_α. The most general such situation is that the $\chi_{i\alpha a}^{(1)}$ will partition into groups. Within each group the $\chi_{i\alpha a}^{(1)}$ will all be connected by a sequence of nonzero $\Lambda_{j\beta b, i\alpha a}^{lm}$. Between groups there will exist no such connection. All the orbitals in a group will have the same $\zeta_{i\alpha}$, which may be different for each group. The most notable example is the all s-orbital Hartree-fock atom (Refs. 1 and 2). See also the discussion by Katriel and Davidson (Ref. 13).

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