

Eigenvalues of Uncorrelated, Density-Difference Matrices and the Interpretation of Δ -Self-Consistent-Field Calculations

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Abstract

Two theorems on the eigenvalues of differences of idempotent matrices determine the natural occupation numbers and orbitals of electronic detachment, attachment or excitation that pertain to transitions between wavefunctions that each consist of a single Slater determinant. They also are applicable to spin-density matrices associated with Slater determinants. When the ranks of the matrices differ, unit eigenvalues occur. In addition, there are $\pm w$ pairs of eigenvalues where $|w| \leq 1$ whose values are related to overlaps, t , between the corresponding orbitals of Amos, Hall and Löwdin by the formula $w = \pm(1 - t^2)^{\frac{1}{2}}$. Generalized overlap amplitudes, including Dyson orbitals and their probability factors, may be inferred from these eigenvalues, which provide numerical criteria for: classifying transitions according to the number of holes and particles in final states with respect to initial states, identifying the most important effects of orbital relaxation produced by self-consistent fields and the analysis of Fukui functions. Two similar theorems that apply to sums of idempotent matrices regenerate formulae for the natural orbitals and occupation numbers of an unrestricted Slater determinant that were published first by Amos and Hall.

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Introduction

Slater determinants have been nearly ubiquitous in the theory and practice of quantum chemistry since the founding decade of this field.¹ Constructing a determinant built of spin-orbitals provided an elegant fulfillment of Pauli's exclusion principle and a foundation for defining and calculating self-consistent-field (SCF), configuration-interaction and other varieties of many-electron wavefunctions.² Many theories without wavefunctions^{3,4} repeatedly have adopted constraints imposed by Slater determinants to prevent problems that arise from a lack of N-representability or deviations from Fermi-Dirac statistics.⁵

Optimization of spin-orbitals according to a variational principle⁶ in Hartree-Fock or Kohn-Sham theories enables the calculation of electron binding energies, excitation energies and corresponding transition probabilities. Δ SCF methods⁷ have proven especially efficient, accurate and lucid in assigning and interpreting core photoelectron spectra of isolated molecules and ions and of cluster models of solids and surfaces.^{8,9} A revival of interest in SCF methods for excited states is based on generalized variational principles¹⁰ or improved algorithms that prevent convergence to ground states.^{11,12} For valence transitions where some of the active spin-orbitals are localized near transition-metal nuclei, Δ SCF methods based on density functionals may be preferable to alternatives that employ a fixed basis optimized only for a reference state. Transitions that involve charge transfers over relatively long distances also may require a flexible approach to spin-orbital relaxation. Determination of double electron binding energies, such as those that are measured in Auger spectra,¹³ may be an even more demanding task in this regard than the calculation of principal, core, ionization energies. Prediction of spectral satellites that correspond in a qualitative sense to multiple changes in spin-orbital occupation numbers is likely to require a full accounting of the effects of relaxation from initial to final states.

To produce reasonable approximations of excited states in SCF calculations, control must be exercised over the spin-orbitals through symmetry restrictions, overlap matching, imposition of additional constraints on Lagrangian functions or other means.^{14,15} Fulfillment of stationarity conditions, usually of the Brillouin type,¹⁶ is the usual criterion of self-consistency, but in some cases this standard cannot be applied.^{17,18} Initial-state and final-state canonical spin-orbitals that satisfy Brillouin and Koopmans¹⁹ conditions may bear little resemblance to each other. The formally canonical spin-orbitals of unrestricted Hartree-Fock theory^{20,21} also may present interpretive challenges that stem from spin contamination. Simple comparisons of canonical spin-orbitals may complicate rather than simplify the task of understanding how electronic structure has changed from one state to another.

The invariance of Slater determinants with respect to linear transformations of their occupied spin-orbitals²² propitiates comparisons between different sets of one-electron functions. Unitary transformations of α and β spin-orbitals produced by a singular-value decomposition of their spatial overlap matrix yields the corresponding orbitals of Amos, Hall and Löwdin.^{23,24} Occupation numbers obtained from unrestricted Hartree-Fock wavefunctions serve as inclusion criteria in unrestricted-natural-orbital, complete-active-space wavefunctions.²⁵ The paired structure of eigenvalues resembles that of perfect-pairing, generalized-valence-bond wavefunctions.²⁶ Corresponding orbitals derived from overlaps obtained for different molecules or for different states of the same molecule have provided succinct generalizations²⁷ of the Slater-Condon rules,^{1,28} facilitated energetic analysis of rotational barriers²⁷ and clarified substituent²⁹ and relaxation³⁰ effects that appear in photoelectron spectra.

Corresponding orbitals are closely related to natural orbitals of an unrestricted, determinantal wavefunction with occupation numbers that may equal unity or may occur in $1 \pm |t|$ pairs, where t is a nonvanishing spatial overlap integral between α and β corresponding orbitals. Natural orbitals with unit occupation numbers equal corresponding orbitals that have no nonvanishing overlaps. Natural orbitals with paired occupation numbers equal normalized sums or differences of pairs of corresponding orbitals with nonvanishing overlaps. Because the α and β spin-orbital-density matrices are guaranteed to have eigenvalues that equal zero or unity by the Slater-determinant Ansatz, the task of obtaining the natural orbitals is equivalent to diagonalizing the sum of two idempotent matrices.

When corresponding orbitals are calculated to enable comparisons between wavefunctions or between the α and β orbitals of a different-orbitals-for-different-spins wavefunction, the overlaps of paired orbitals are the chief criteria of similarity. In Δ SCF calculations of electron-binding energies, an unpaired corresponding orbital may be understood as having been added or removed, for its occupation number changes from zero to unity or vice versa. A more thorough analysis of differences between states, molecules or spin-component densities can be procured by examining differences of the corresponding idempotent matrices.

Toward this end, two theorems that determine the eigenvalues of the sum of two idempotent matrices and that deepen and confirm the conclusions of Amos and Hall²³ are followed by two additional theorems that perform the same function for the difference of two idempotent matrices. In both cases, corresponding orbitals are essential intermediates in deriving the eigenvalues.

Eigenvalues of the *sum* of the idempotent α and β density matrices derived from a Slater determinant define the natural occupation numbers of this wavefunction. Theorem 1 reveals the structure of the eigenvalue spectrum for the overlap matrix between α and β corresponding orbitals. Theorem 2 demonstrates that these eigenvalues are also eigenvalues of the sum of the α and β density matrices. Subsequent discussion considers formulae that relate overlaps between α and β corresponding orbitals to natural orbitals, their occupation numbers, density matrices and the S^2 criterion of spin contamination. Table 1 and equation 39 summarize these conclusions, which confirm those of Amos and Hall. These theorems are equally applicable to any sum of idempotent matrices.

Theorems 3 and 4 employ arguments that resemble those of Theorems 1 and 2 and consider *differences* of idempotent matrices. Theorem 3 yields the eigenvalue spectrum of a matrix with off-diagonal blocks that contain overlaps between two sets (e.g. α and β , initial-state and final-state) of corresponding orbitals. Theorem 4 shows that these eigenvalues are also eigenvalues of the difference of idempotent density matrices. The discussion that follows explicitly relates overlaps between sets of corresponding orbitals and natural orbitals, occupation numbers and density matrices that characterize differences between initial and final states of ionization or excitation. These relationships also are applicable to spin densities. Table 2 and equation 59 summarize these conclusions.

Dyson orbitals, their probability factors, Fukui functions (ground-state, electron-density differences) and changes in orbital occupation numbers that accompany single-determinant descriptions of transitions in which an electron is detached or attached are considered next. Formulae that relate overlaps between sets of corresponding orbitals to probability factors and Fukui functions are given. Table 3 summarizes these results. Extensions of these concepts to excitations or multiple electron detachments and

attachments are the subject of an additional section. The Conclusion section reviews the manifold implications of this study and their common origins in Theorems 3 and 4.

Eigenvalues of the sum of two idempotent matrices

The following two theorems provide a generalized route to the principal conclusions of Amos and Hall²³ that apply to the eigenvalues of any sum of two idempotent matrices. In addition, they suggest an approach to the subsequent problem that pertains to differences of idempotent matrices.

Theorem 1

Let $T = (t_{i,j}; i = 1, \dots, p; j = 1, \dots, q)$ be a $p \times q$ matrix with $p \geq q$ and such that $i \neq j$ implies that $t_{i,j} = 0$, let ℓ and δ respectively denote the number of 0's and 1's in the sequence $(|t_{j,j}|; j = 1, \dots, q)$, let $n = p + q$, and let M be one of the following $n \times n$ matrices:

$$M_1 = \begin{pmatrix} I_p & T \\ T^\dagger & I_q \end{pmatrix} \quad (1)$$

$$M_2 = \begin{pmatrix} I_p & -T \\ -T^\dagger & I_q \end{pmatrix}. \quad (2)$$

Then:

- (a) 1 is an eigenvalue of M with multiplicity $p - q + 2\ell$, provided that $p > q$ or $\ell > 0$. In particular, if $\ell = q$, then $T = 0$; therefore in this case 1 is the only eigenvalue of M and its multiplicity is n .
- (b) If $\delta > 0$, then 0 and 2 are eigenvalues of M , each with multiplicity δ . Conversely, if either 0 or 2 are eigenvalues of M then $\delta > 0$, both 0 and 2 are eigenvalues of M , and both have multiplicity δ , but if $\delta = 0$, then neither 0 nor 2 are eigenvalues of M .
- (c) All eigenvalues of M different from 0, 1 and 2, if any, are of the form $1 \pm s_r, r = 1, \dots, q - (\ell + \delta)$, where the s_r are those $|t_{j,j}|$ that are not equal to 0 or 1.
- (d) All eigenvalues of M different from 0, 1 and 2 will have multiplicity not exceeding $q - (\ell + \delta)$.

Proof:

If $\ell = \delta$ then $t_{j,j} = 0, j = 1, \dots, q$, and therefore $T = 0$. Let $T \neq 0$, and assume first that $M = M_1$.

Define

$$E_1 = \begin{pmatrix} (\lambda - 1)I_p & 0 \\ T^\dagger & I_q \end{pmatrix} \quad (3)$$

and $F_1 = (\lambda I_n - M_1)E_1$. Then, since E_1 is a block triangular matrix we have

$$\det(F_1) = (\lambda - 1)^p \det(\lambda I_n - M_1). \quad (4)$$

(cf. Horn and Johnson).³¹ But

$$F_1 = \begin{pmatrix} (\lambda-1)^2 I_p - TT^\dagger & -T \\ 0 & (\lambda-1)I_q \end{pmatrix}. \quad (5)$$

Therefore

$$\det(F_1) = (\lambda-1)^q \det((\lambda-1)^2 I_p - TT^\dagger). \quad (6)$$

By hypothesis we know that $t_{i,j} = 0$ if $i \neq j$. Note that $i = j$ only for $j = 1, \dots, q$, since that is the range of j . By a straightforward computation we therefore conclude that the entries $c_{i,j}$ of the $p \times p$ matrix TT^\dagger are such that $c_{i,j} = 0$ if $i \neq j$ or, if $p > q$, if $i = j$ and $j = q+1, \dots, p$, and that $c_{j,j} = |t_{j,j}|^2$ for $j = 1, \dots, q$.

This implies that

$$(\lambda-1)^2 I_p - TT^\dagger = \text{diag}((\lambda-1)^2 - c_{j,j}; j = 1, \dots, p), \quad (7)$$

and therefore that

$$\det((\lambda-1)^2 I_p - TT^\dagger) = (\lambda-1)^{2(p-q)} \prod_{j=1}^q ((\lambda-1)^2 - |t_{j,j}|^2). \quad (8)$$

Thus

$$\det(F_1) = (\lambda-1)^{2p-q} \prod_{j=1}^q ((\lambda-1)^2 - |t_{j,j}|^2), \quad (9)$$

and from equation 4 we deduce that

$$\det(\lambda I_n - M_1) = (\lambda-1)^{p-q} \prod_{j=1}^q ((\lambda-1)^2 - |t_{j,j}|^2) = (\lambda-1)^{p-q+2\ell} \lambda^\delta (\lambda-2)^\delta \prod_{r=1}^{q-(\ell+\delta)} ((\lambda-1)^2 - s_r^2). \quad (10)$$

where the s_r are those $|t_{j,j}|$ that are not equal to 0 or 1. Assume now that $M = M_2$, and let

$$E_2 = \begin{pmatrix} (\lambda-1)I_p & 0 \\ -T^\dagger & I_q \end{pmatrix} \quad (11)$$

and $F_2 = (\lambda I_n - M_2)E_2$. Then

$$\det(F_2) = (\lambda-1)^p \det(\lambda I_n - M_2). \quad (12)$$

But

$$F_2 = \begin{pmatrix} (\lambda-1)^2 I_p - TT^\dagger & T \\ 0 & (\lambda-1)I_q \end{pmatrix}. \quad (13)$$

Thus $\det(F_2)$ equals the right hand side of equation 9, and therefore equation 12 implies that $\det(\lambda I_n - M_2)$ equals the right-hand side of equation 10, whence the assertion follows. \square

Theorem 2

Let A be an $m \times p$ matrix with no zero columns and with mutually orthogonal columns and let B be an $m \times q$ matrix with no zero columns and with mutually orthogonal columns. Assume that $p \geq q$ and $m \geq n$ and define $P = AA^\dagger$ and $Q = BB^\dagger$. Let $U_1 S V_1^\dagger = T$, where $T = (t_{i,j})$ is a diagonal matrix, be the singular value decomposition of $S = A^\dagger B$ (whence the $t_{i,i}$ are nonnegative and listed in decreasing order of magnitude), let ℓ and δ respectively denote the number of 0's and 1's in the sequence $(t_{j,j}; j = 1, \dots, q)$, and let $n = p + q$. Then the eigenvalues of P are 1 with multiplicity p and 0 with multiplicity $m - p$, the eigenvalues of Q are 1 with multiplicity q and 0 with multiplicity $m - q$, and:

(a) 1 is an eigenvalue of M with multiplicity $p - q + 2\ell$, provided that $p > q$ or $\ell > 0$. In particular, if $\ell = q$, then $T = 0$; therefore in this case 1 is the only eigenvalue of M and its multiplicity is n .

(b) 0 is an eigenvalue of $P + Q$ with multiplicity $m - n + \delta$, provided that $m > n$ or $\delta > 0$.

(c) 2 is an eigenvalue of $P + Q$ with multiplicity δ , provided that $\delta > 0$.

(d) All eigenvalues of $P + Q$, different from 0, 1 and 2 are of the form $1 \pm s_r$, $r = 1, \dots, q - (\ell + \delta)$, where the s_r are those $t_{j,j}$ that are not equal to 0 or 1.

(e) If in addition to the hypotheses, every column of A is perpendicular to every column of B , then 1 is the only eigenvalue of $P + Q$, and its multiplicity is n .

Proof:

Note that $P^2 = (AA^\dagger)(AA^\dagger) = A I_p A^\dagger = P$ and similarly $Q^2 = Q$. Thus P and Q are idempotent and therefore their eigenvalues are either 0 or 1. The hypotheses imply that $A^\dagger A = I_p$ and $B^\dagger B = I_q$. Since (see 2, 1.3.22)³¹ implies that $A^\dagger A$ and AA^\dagger have the same nonzero eigenvalues including multiplicities, and the trace of a matrix equals the sum of all its eigenvalues (cf. 2, p. 50),³¹ we deduce that $\text{tr}(AA^\dagger) = \text{tr}(A^\dagger A) = p$, i.e. $\text{tr}(P) = p$ and similarly $\text{tr}(Q) = q$. Since the nonzero eigenvalues can only equal 1, the multiplicity follows.

Let C be the $m \times n$ partitioned matrix defined by $C = (A, B)$; then

$$CC^\dagger = (A, B) \begin{pmatrix} A^\dagger \\ B^\dagger \end{pmatrix} = AA^\dagger + BB^\dagger = P + Q \quad (14)$$

and

$$C^\dagger C = \begin{pmatrix} A^\dagger \\ B^\dagger \end{pmatrix} (A, B) = \begin{pmatrix} I_p & S \\ S^\dagger & I_q \end{pmatrix}, \quad (15)$$

where $S = A^\dagger B$. Note that if in addition to the hypotheses, every column of A is perpendicular to every column of B then $S = 0$ and the assertion of (e) follows. In the general case we proceed as follows: since the p rows of A^\dagger are mutually orthogonal, we deduce that $\text{rank}(A^\dagger) = p$; thus it has a nonsingular $p \times p$ submatrix A_1 .³¹ We deduce that $\text{rank}(A_1 B) = \text{rank}(B) = q$.³¹ Therefore, $\text{rank}(B^\dagger A) = \text{rank}(A^\dagger B) = q$.³¹ Note that $B^\dagger A$ is a $q \times p$ matrix. Since $p \geq q$, applying the theorem

in Amos and Hall's Appendix²³ or Theorem 2.6.3 of Horn and Johnson,³¹ we obtain the singular value decomposition of S : there are unitary matrices U and V such that $USV = T$, where $T = (t_{i,j})$ is such that $i \neq j$ implies that $t_{i,j} = 0$. If the diagonal elements of T are listed in decreasing order, this representation is unique. Thus

$$\begin{pmatrix} U^\dagger & 0 \\ 0 & V^\dagger \end{pmatrix} \begin{pmatrix} I_p & S \\ S^\dagger & I_q \end{pmatrix} \begin{pmatrix} U & 0 \\ 0 & V \end{pmatrix} = \begin{pmatrix} I_p & T \\ T^\dagger & I_q \end{pmatrix}, \quad (16)$$

Since CC^\dagger and $C^\dagger C$ have the same nonzero eigenvalues including multiplicities,³¹ the assertion follows from Theorem 1. \square

Discussion

Amos and Hall²³ were concerned with unrestricted Hartree-Fock wavefunctions^{20, 21} wherein $N_\alpha \alpha$ orbitals and $N_\beta \beta$ orbitals (with $N_\alpha \geq N_\beta$) are expressed in an orthonormal basis of m functions ($\omega_s, s = 1, \dots, m$) such that

$$\psi_r^\alpha = \sum_{s=1}^m \omega_s A_{sr}, \quad r = 1, \dots, N_\alpha \quad (17)$$

$$\psi_r^\beta = \sum_{s=1}^m \omega_s B_{sr}, \quad r = 1, \dots, N_\beta. \quad (18)$$

The α and β orbital-density matrices, \mathbf{P} and \mathbf{Q} ,

$$\mathbf{P} = \mathbf{A}\mathbf{A}^\dagger \quad (19)$$

$$\mathbf{Q} = \mathbf{B}\mathbf{B}^\dagger \quad (20)$$

are idempotent such that

$$\mathbf{P}^2 = \mathbf{P} \quad (21)$$

$$\mathbf{Q}^2 = \mathbf{Q} \quad (22)$$

and their traces equal the number of electrons of each spin, where

$$\text{Tr}\mathbf{P} = p = N_\alpha \quad (23)$$

$$\text{Tr}\mathbf{Q} = q = N_\beta. \quad (24)$$

The orthonormality of the spin-orbitals implies that

$$\mathbf{A}^\dagger \mathbf{A} = \mathbf{I}_p \quad (25)$$

$$\mathbf{B}^\dagger \mathbf{B} = \mathbf{I}_q, \quad (26)$$

but the non-orthogonality of the two sets of orbitals results in a rectangular overlap matrix, \mathbf{S} , given by

$$\mathbf{A}^\dagger \mathbf{B} = \mathbf{S}. (27)$$

After defining \mathbf{C} to be a matrix with $p + q$ columns, where

$$\mathbf{C} = [\mathbf{A} \quad \mathbf{B}], (28)$$

the product $\mathbf{C}^\dagger \mathbf{C}$ has the following block structure:

$$\mathbf{C}^\dagger \mathbf{C} = \begin{bmatrix} \mathbf{I}_p & \mathbf{S} \\ \mathbf{S}^\dagger & \mathbf{I}_q \end{bmatrix}. (29)$$

Unitary transformations of the α and β orbitals that define the corresponding orbitals,

$$\phi_r^\alpha = \sum_{s=1}^{N_\alpha} \psi_s^\alpha U_{sr} (30)$$

$$\phi_r^\beta = \sum_{s=1}^{N_\beta} \psi_s^\beta V_{sr}, (31)$$

are produced in the singular-value decomposition of the overlap matrix,

$$\mathbf{U}^\dagger \mathbf{S} \mathbf{V} = \mathbf{T}, (32)$$

where \mathbf{T} is a rectangular, diagonal matrix of overlaps between α and β corresponding orbitals. There are $p - q$ corresponding orbitals in the α set that are orthogonal to the β orbitals and q pairs of α and β corresponding orbitals with maximized overlaps. The elements of the new, overlap matrix in the corresponding-orbital basis, \mathbf{T} , read

$$T_{rs} = \delta_{rs} T_{rr}. (33)$$

In the singular value decomposition of T , the nonzero $t_{i,i}$'s are the positive square roots of the nonzero eigenvalues of TT^\dagger , which are the same as the nonzero eigenvalues of $T^\dagger T$. The number of diagonal elements with absolute values of zero and one are denoted respectively by ℓ and δ . In the corresponding orbital basis, $\mathbf{C}^\dagger \mathbf{C}$ has fewer non-zero elements, for

$$\begin{bmatrix} \mathbf{U}^\dagger & \mathbf{0} \\ \mathbf{0} & \mathbf{V}^\dagger \end{bmatrix} \mathbf{C}^\dagger \mathbf{C} \begin{bmatrix} \mathbf{U} & \mathbf{0} \\ \mathbf{0} & \mathbf{V} \end{bmatrix} = \begin{bmatrix} \mathbf{I}_p & \mathbf{T} \\ \mathbf{T}^\dagger & \mathbf{I}_q \end{bmatrix}. (34)$$

The eigenvalues of $\mathbf{C}^\dagger \mathbf{C}$ and their multiplicities (i.e. degeneracies) are given by Theorem 1. $\mathbf{C} \mathbf{C}^\dagger$ has the same eigenvalues and multiplicities and, in addition, $m - (p + q)$ eigenvalues that equal zero.²³ Because

$$\mathbf{C} \mathbf{C}^\dagger = \mathbf{A} \mathbf{A}^\dagger + \mathbf{B} \mathbf{B}^\dagger = \mathbf{P} + \mathbf{Q}, (35)$$

the eigenvalues of the sum of the idempotent α and β orbital-density matrices may be summarized in Table 1, where the last two columns refer to the paired eigenvalues that are not equal to those of the three preceding columns.

INSERT TABLE 1 HERE

Deviations of the corresponding-orbital overlaps from unity are evidence of spin contamination. In this basis, the difference between the exact expectation value of S^2 and its unrestricted, Hartree-Fock counterpart reads

$$\langle S^2 \rangle_{exact} - \langle S^2 \rangle_{UHF} = N_\beta - \sum_{r=1}^{N_\beta} t_{rr}^2. \quad (36)$$

The deviations vanish only when all the overlaps equal unity.

After defining the normalized sums and differences of pairs of overlapping corresponding orbitals according to

$$\mu_r(1) = (2 + 2t_{rr})^{-\frac{1}{2}} [\phi_r^\alpha(1) + \phi_r^\beta(1)] \quad (37)$$

$$v_r(1) = (2 - 2t_{rr})^{-\frac{1}{2}} [\phi_r^\alpha(1) - \phi_r^\beta(1)], \quad (38)$$

the spin-integrated density matrix reads

$$\rho(1|1') = \sum_{r=1}^{p-q} \phi_r^\alpha(1) \phi_r^{\alpha*}(1') + \sum_{r=1}^q [(1+t_{rr})\mu_r(1)\mu_r^*(1') + (1-t_{rr})v_r(1)v_r^*(1')], \quad (39)$$

where the ϕ , μ and v functions constitute an orthogonal set of natural orbitals. There are $N_\alpha - N_\beta$ unpaired, high-spin contributions to the first term from corresponding orbitals. N_β pairs of natural orbitals are present in the second term.

Eigenvalues of the difference of two idempotent matrices

Two theorems that employ similar strategies as those of the previous section apply to the eigenvalues of any difference of two idempotent matrices.

Theorem 3

Under the same assumptions and with the same definitions as in Theorem 1, let

$$M_3 = \begin{pmatrix} I_p & -T \\ T^\dagger & -I_q \end{pmatrix} \quad (40)$$

Then:

(a) All real eigenvalues of M_3 are on the interval $[-1, 1]$.

- (b) -1 is an eigenvalue of M_3 with multiplicity ℓ , provided that $\ell > 0$. In particular, if $\ell = q$ then $T = 0$ and therefore in this case the only eigenvalues of M_3 are -1 , with multiplicity q , and 1 , with multiplicity p .
- (c) 0 is an eigenvalue of M_3 with multiplicity 2δ , provided that $\delta > 0$.
- (d) 1 is an eigenvalue of M_3 with multiplicity $p - q + \ell$, provided that $p > q$ or $\ell > 0$.
- (e) All eigenvalues of M_3 different from $-1, 0$ and 1 , if any, may be complex-valued and are of the form $\pm(1 - (s_r)^2)^{1/2}$, $r = 1, \dots, q - (\ell + \delta)$, where the s_r are those $t_{j,j}$ that are not equal to 0 or 1 .
- (f) All eigenvalues of M_3 different from $-1, 0$ and 1 , if any, will have multiplicities not exceeding q . If -1 is an eigenvalue of M_3 its multiplicity will equal ℓ and may not exceed q ; if 0 is an eigenvalue of M_3 its multiplicity will equal 2δ and may not exceed $2q$; if 1 is an eigenvalue of M_3 its multiplicity will equal $p - q + \ell$ and may not exceed p .

Proof:

Assume that $T \neq 0$. Let

$$E_3 = \begin{pmatrix} I_p & -T \\ 0 & (\lambda - 1)I_q \end{pmatrix} \quad (41)$$

and $F_3 = (\lambda I_n - M_3)E_3$. Then

$$\det(F_3) = (\lambda - 1)^q \det(\lambda I_n - M_3). \quad (42)$$

But

$$F_3 = \begin{pmatrix} (\lambda - 1)I_p & 0 \\ -T^\dagger & T^\dagger T + (\lambda^2 - 1)I_q \end{pmatrix}. \quad (43)$$

Therefore, we also have

$$\det(F_3) = (\lambda - 1)^p \det(T^\dagger T + (\lambda^2 - 1)I_q), \quad (44)$$

whence

$$\det(F_3) = (\lambda - 1)^p \prod_{j=1}^q (\lambda^2 - 1 + |t_{j,j}|^2). \quad (45)$$

Thus, from equation 42 we deduce that

$$\det(\lambda I_n - M_3) = (\lambda - 1)^{p-q} \prod_{j=1}^p (\lambda^2 - 1 + |t_{j,j}|^2) = (\lambda - 1)^{p-q} (\lambda^2 - 1)^\ell \lambda^{2\delta} \prod_{r=1}^{q-\ell-\delta} (\lambda^2 - 1 + (s_r)^2). \quad (46)$$

To find the bounds for $-1, 0$ and 1 in (f) note that ℓ and δ are bounded by q . The preceding equation shows that if λ is an eigenvalue other than $-1, 0$ or 1 , then $\lambda^2 = 1 - (s_r)^2$, where s_r is one of the $t_{j,j}$ that is not equal to 0 or 1 . Since $(s_r)^2$ could be larger than 1 , it follows that λ^2 could be negative and

that λ may be complex-valued, whence (e) follows. The remaining assertions are straightforward consequences of equation 46. \square

Theorem 4

Let A be an $m \times p$ matrix with no zero columns and with mutually orthogonal columns and let B be an $m \times q$ matrix with no zero columns and with mutually orthogonal columns. Assume that $p \geq q$ and $m \geq n$ and define $P = AA^\dagger$ and $Q = BB^\dagger$. Let $U_1 S V_1 = T$, where $T = (t_{i,j})$ is a diagonal matrix, be a singular value decomposition of $S = A^\dagger B$ (whence the $t_{i,i}$ are nonnegative and listed in decreasing order of magnitude), let ℓ and δ respectively denote the number of 0's and 1's in the sequence $(t_{j,j}; j = 1, \dots, q)$, and let $n = p + q$. Then:

- (a) Every eigenvalue of $P - Q$ is real and is on the interval $[-1, 1]$.
- (b) -1 is an eigenvalue of $P - Q$ with multiplicity ℓ , provided that $\ell > 0$. In particular, if $\ell = q$ then $T = 0$ and therefore the only eigenvalues of $P - Q$ in this case are -1 , with multiplicity q , and 1 , with multiplicity p .
- (c) 0 is an eigenvalue of $P - Q$ with multiplicity $m - n + 2\delta$, provided that $m - n + 2\delta > 0$.
- (d) 1 is an eigenvalue of $P - Q$ with multiplicity $p - q + \ell$, provided that $p > q$ or $\ell > 0$.
- (e) All eigenvalues of $P - Q$ different from $-1, 0$ and 1 , if any, are of the form $\pm(1 - (s_r)^2)^{1/2}$, $r = 1, \dots, q - (\ell + \delta)$, where the s_r are those $t_{j,j}$ that satisfy the inequalities $0 < |t_{j,j}| < 1$.
- (f) All eigenvalues of $P - Q$ different from $-1, 0$ and 1 , if any, will have multiplicities not exceeding q . If -1 is an eigenvalue of $P - Q$ its multiplicity will equal ℓ and may not exceed q ; if 0 is an eigenvalue of $P - Q$ its multiplicity will equal 2δ and may not exceed $2q$; if 1 is an eigenvalue of $P - Q$ its multiplicity will equal $p - q + \ell$ and may not exceed p .
- (g) If in addition to the hypotheses, every column of A is perpendicular to every column of B , then the only eigenvalues of $P - Q$ are -1 with multiplicity q , and 1 with multiplicity p .

Proof:

Note that since $P - Q$ is Hermitian all its eigenvalues are real. Let

$$D_1 = (A, -B) \begin{pmatrix} A^\dagger \\ B^\dagger \end{pmatrix} = AA^\dagger - BB^\dagger = P - Q \quad (47)$$

and let

$$D_2 = \begin{pmatrix} A^\dagger \\ B^\dagger \end{pmatrix} (A, -B) = \begin{pmatrix} I_p & -S \\ S^\dagger & -I_q \end{pmatrix}, \quad (48)$$

where $S = A^\dagger B$. If in addition to the hypotheses, every column of A is perpendicular to every column of B , then $S = 0$ and the assertion of (g) follows. In the general case, as in the proof of Theorem 2 we know that there are unitary matrices U and V such that $USV = T$, where $T = (t_{i,j})$ is such that $i \neq j$ implies that $t_{i,j} = 0$. Thus

$$\begin{pmatrix} U^\dagger & 0 \\ 0 & V^\dagger \end{pmatrix} \begin{pmatrix} I_p & -S \\ S^\dagger & -I_q \end{pmatrix} \begin{pmatrix} U & 0 \\ 0 & V \end{pmatrix} = \begin{pmatrix} I_p & -T \\ T^\dagger & -I_q \end{pmatrix}. \quad (49)$$

Since D_1 and D_2 have the same nonzero eigenvalues and $D_1 = P - Q$, the assertion follows from Theorem 3. In particular, note that if λ is an eigenvalue of $P - Q$ other than $-1, 0$ or 1 , then $\lambda^2 = 1 - (s_r)^2$, where s_r is one of the $t_{j,j}$ that is not equal to 0 or 1 . Since, as noted before, all the eigenvalues of $P - Q$ must be real, we conclude that $0 < (s_r)^2 < 1$, and (e) follows. \square

Discussion

After defining C_1 and C_2 by

$$C_1 = [\mathbf{A} \quad -\mathbf{B}] \quad (50)$$

and

$$C_2 = \begin{bmatrix} \mathbf{A}^\dagger \\ \mathbf{B}^\dagger \end{bmatrix} \quad (51)$$

the product $C_2 C_1$ has the following block structure:

$$C_2 C_1 = \begin{bmatrix} \mathbf{I}_p & -\mathbf{S} \\ \mathbf{S}^\dagger & -\mathbf{I}_q \end{bmatrix}. \quad (52)$$

Transformation to the corresponding orbitals yields

$$\begin{bmatrix} U^\dagger & \mathbf{0} \\ \mathbf{0} & V^\dagger \end{bmatrix} C_2 C_1 \begin{bmatrix} U & \mathbf{0} \\ \mathbf{0} & V \end{bmatrix} = \begin{bmatrix} \mathbf{I}_p & -\mathbf{T} \\ \mathbf{T}^\dagger & -\mathbf{I}_q \end{bmatrix}. \quad (53)$$

The eigenvalues of $C_2 C_1$ and their multiplicities (i.e. degeneracies) are given by Theorem 3. $C_1 C_2$ has the same eigenvalues and multiplicities and, in addition, $M - (p + q)$ eigenvalues that equal zero.²³

Because

$$C_1 C_2 = \mathbf{A} \mathbf{A}^\dagger - \mathbf{B} \mathbf{B}^\dagger = \mathbf{P} - \mathbf{Q}, \quad (54)$$

the eigenvalues of the difference of the idempotent α and β orbital-density matrices may be summarized in Table 2, where the last two columns refer to the paired eigenvalues that are not equal to integers. Whereas the results of the previous section pertain to the charge density, those of this section pertain to the spin density.

INSERT TABLE 2 HERE

After defining the normalized, symmetrically orthogonalized³² combinations of pairs of overlapping corresponding orbitals according to

$$\kappa_r(1) = a_r \phi_r^\alpha(1) + b_r \phi_r^\beta(1) \quad (55)$$

$$\lambda_r(1) = b_r \phi_r^\alpha(1) + a_r \phi_r^\beta(1), \quad (56)$$

where

$$a_r = \frac{1}{2} (\sqrt{1+|t_{rr}|} + \sqrt{1-|t_{rr}|}) \quad (57)$$

$$b_r = \frac{1}{2} (\sqrt{1+|t_{rr}|} - \sqrt{1-|t_{rr}|}), \quad (58)$$

the spin-integrated, density-difference matrix reads

$$\Delta\rho(1|1') = \sum_{r=1}^{p-q} \phi_r^\alpha(1) \phi_r^{\alpha*}(1') + \sum_{r=1}^q \left[\sqrt{1-t_{rr}^2} \kappa_r(1) \kappa_r^*(1') - \sqrt{1-t_{rr}^2} \lambda_r(1) \lambda_r^*(1') \right], \quad (59)$$

where the ϕ, κ and λ functions constitute an orthogonal set of natural orbitals. The first summation has $N_\alpha - N_\beta$ terms that involve unpaired, corresponding orbitals. N_β pairs of natural orbitals occur in the second summation.

Dyson Orbitals, Probability Factors and Fukui Functions

Electron-binding energies calculated as differences of initial-state (N-electron) and final-state (N ± 1-electron) energies evaluated variationally with Slater determinants may be based on a fixed set of spin-orbitals, as in Koopmans's identity,¹⁹ or may include the effects of orbital relaxation, as in the Δ SCF method.⁷ For final-state energies, the Koopmans result provides an upper bound to the SCF value. The former approximation represents the effects of kinetic, Coulombic and exchange terms in electron-binding energies that are associated with the electronic structure of the initial state. Differences between Koopmans and Δ SCF results arise because of changes in the occupied spin-orbitals of the final state.

Dyson spin-orbitals of electron detachment and attachment from an initial state (Ψ_I) to a final state (Ψ_F) are defined respectively by the following two equations:

$$\varphi_{FI}^{Dyson}(x_1) = \sqrt{N} \int \Psi_F^*(x_2, x_3, x_4, \dots, x_N) \Psi_I(x_1, x_2, x_3, \dots, x_N) dx_2 dx_3 dx_4 \dots dx_N \quad (60)$$

$$\varphi_{IF}^{Dyson}(x_1) = \sqrt{N+1} \int \Psi_I^*(x_2, x_3, x_4, \dots, x_{N+1}) \Psi_F(x_1, x_2, x_3, \dots, x_{N+1}) dx_2 dx_3 dx_4 \dots dx_{N+1}, \quad (61)$$

where x_z is the space-spin coordinate of electron z . 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

$$0 \leq P_{IF} = \int dx |\varphi_{IF}^{Dyson}(x)|^2 \leq 1. \quad (62)$$

Transition probabilities in the sudden approximation^{33, 34} are proportional to probability factors.

When a closed-shell, Hartree-Fock wavefunction approximates the initial state and the frozen-orbital approximation of Koopmans's identity is made for the final state, the Dyson spin-orbital equals a canonical, Hartree-Fock spin-orbital and the probability factor equals unity. These conclusions may be extended formally to cases where an unrestricted Hartree-Fock wavefunction is chosen for the initial state and frozen-orbital approximations are made for final states. When the initial and final states are well represented by single Slater determinants and spin contamination is low, this formal extension is potentially useful. An alternative that eliminates spin contamination is provided by restricted, open-shell Hartree-Fock (ROHF) wavefunctions and their canonical orbitals that pertain to high-spin final states.^{35, 36} In these cases, overlaps between initial and final spin-orbitals are equal to zero or unity and therefore there is only one natural ionization orbital³⁷ (i.e. an eigenfunction of the density-difference matrix) with a non-vanishing eigenvalue. For some final states of low spin, more than one Slater determinant is needed to construct a spin eigenstate; a single-determinant approximation, having components of more than one multiplicity, will be spin-contaminated. For example, removal of an α electron from the $1s$ orbital of the doublet ROHF wavefunction of ground-state CH_3 with $M_S = \frac{1}{2}$ yields a final-state determinant that is half singlet and half triplet. Some expressions for orbital energies provide electron binding energies that are averaged over more than one final state.³⁸

Evaluation of the Dyson spin-orbital that pertains to Δ SCF calculations is facilitated by expressing Slater determinants in terms of corresponding spin-orbitals that arise from the singular-value decomposition of the overlap matrix between initial-state and final-state spin-orbitals. (Note that previously discussed procedures for determining charge or spin densities and their sum or difference density matrices required overlaps between α and β orbitals of the Slater determinant of a single state.) The Dyson spin-orbital is proportional to the unpaired, corresponding spin-orbital which is also the natural ionization spin-orbital with an eigenvalue of unity. Non-integer eigenvalues of differences of idempotent, orbital-density matrices for α and β spin provide information about orbital relaxation. The $N-1$ or N integrations in the two definitions of the Dyson spin-orbitals produce a non-vanishing term only when there are no permutationally induced mismatches between the paired, corresponding spin-orbitals. The Dyson spin-orbital therefore equals the unpaired, corresponding spin-orbital times the product of the overlap matrices of the paired spin-orbitals. For electron detachments, the probability factor equals the product of the squares of the $N-1$ overlaps between initial-state and final-state orbitals and is related by Theorem 4 to the $N-1$ ($\pm w$) pairs of density-difference eigenvalues by

$$P = \prod_{r=1}^{N-1} t_{rr}^2 = \prod_{r=1}^{N-1} (1 - w_r^2). \quad (63)$$

The appearance of paired eigenvalues has been amply confirmed in numerical calculations of natural ionization orbitals.³⁷ For electron-binding energies where the Koopmans description is qualitatively valid, values of w will be close to zero. If one or more of the overlaps between sets of corresponding orbitals approaches zero, pairs of density-difference eigenvalues that approach ± 1 will appear. This diagnostic is characteristic of a shake-up (correlation) final state for which the probability factor will be close to zero. Partial re-optimizations of final-state orbitals with respect to their initial-state counterparts which may be undertaken to analyze relaxation effects can result in corresponding-orbital overlaps of unity and concomitant, additional zero eigenvalues of density-difference matrices.

In Koopmans and Δ SCF calculations with non-zero probability factors, the occupation number of a single spin-orbital (i.e. the expectation value of its number operator) changes from unity to zero for electron detachments and from zero to unity for electron attachments. No other changes in occupation numbers occur at the Koopmans level of theory, but Δ SCF calculations allow occupation numbers of the other initial-state spin-orbitals to change from 1 or 0 to other values in the final state.

These simple rules disappear when initial and final states are correlated. For example, in electron propagator calculations with full or diagonal (in the canonical, Hartree-Fock basis) self-energy (Σ) matrices,^{3, 39, 40} changes in occupation numbers associated with density-difference matrices^{41, 42} usually do not equal integers. Such calculations do not, in general, capture all of the orbital relaxation that occurs in Δ SCF calculations, but aim instead for a balanced treatment of many-body effects. Self-energy approximations that supplement Δ SCF results with selected terms that pertain only to initial-state and final-state correlation have been applied to the calculation of electron affinities.^{43, 44} A summary of Dyson orbitals expressed in terms of canonical Hartree-Fock (ψ) or corresponding (ϕ) orbitals, probability factors and changes in occupation numbers that emerge in various levels of theory appears in Table 3.

INSERT TABLE 3 HERE

Δ SCF Dyson orbitals may be expressed as a linear combination of occupied orbitals according to equations 30 and 31, but exact Dyson orbitals involve summations over all (occupied or virtual) orbitals. Probability factors of unity and changes of ± 1 in occupation numbers at the Koopmans and Δ SCF levels of theory indicate that an electron assigned to a Dyson orbital is unambiguously annihilated or created for final states with N-1 or N+1 electrons, respectively. Such certainty is abolished at higher levels of theory. Changes in occupation numbers of non-Dyson orbitals vanish only at the Koopmans (i.e. frozen-orbital) level.

Whereas the Koopmans approximation produces a single, non-vanishing eigenvalue of unity for the density-difference matrix, the accompanying electron-density differences pertaining to the lowest electron detachment energy or the largest electron attachment energy, also known as Fukui functions,⁴⁵ have positive values at all points in space. Negative values of a detachment or attachment Fukui function,⁴⁶ f^{Fukui} , become possible in Δ SCF calculations, for negative eigenvalues of the density-difference matrix will usually appear. Such an outcome can become more likely when non-zero overlaps between paired corresponding orbitals are low due to spatial separation, leading to one or more large λ terms in the summation below:

$$f^{Fukui}(1) = |\phi(1)|^2 + \sum_{r=1}^q \left[\sqrt{1-t_{rr}^2} |\kappa_r(1)|^2 - \sqrt{1-t_{rr}^2} |\lambda_r(1)|^2 \right]. \quad (64)$$

Negative spin-densities may appear for similar reasons in SCF calculations on a single state or in Δ SCF calculations wherein differences of α or β density matrices are evaluated.

Other Classes of Transitions

Double or multiple electron-binding energies corresponding to initial and final states that are well-approximated by single Slater determinants, such as transitions to triplets with two open shells that are

measured in Auger spectroscopy¹³ on closed-shell molecules, give rise to two or more density-difference eigenvalues of unity. The accompanying unpaired orbitals may be used to construct Slater determinants that define Dyson geminals or multiple-electron-overlap amplitudes. One can expect the values of w that occur in the remaining pairs of $\pm w$ eigenvalues to become larger and thereby reflect the enhanced importance of orbital relaxation when two or more electrons are added or removed.

Several classes of excitation energies correspond to initial-state and final-state wavefunctions that are well represented by lone Slater determinants. Excitations from a closed-shell initial state to a triplet with two open shells will produce unpaired α natural excitation orbitals with accompanying relaxation effects represented by corresponding sets of paired orbitals. Examples include core-valence and charge-transfer excitations. Doublet radicals with SOMO-LUMO or HOMO-SOMO (SO = singly occupied, HO = highest doubly occupied, LU = lowest unoccupied, MO = molecular orbital) transitions will have paired orbitals that pertain to eigenvalues near ± 1 when relaxation effects are weak and overlaps between the two, main, corresponding orbitals are close to zero. The sums of positive (or negative) eigenvalues that pertain to the natural excitation orbitals⁴⁷ (i.e. natural transition orbitals where the number of electrons in the transition is conserved) are qualitative indices that may distinguish between singly or doubly excited states.⁴⁸

Conclusions

Unit and paired eigenvalues of spin-density and density-difference matrices that emerge from determinantal wavefunctions are effects of a common cause: diagonalization of the difference of two, idempotent matrices. Singular-value decompositions of overlap matrices between orbitals that underlie two, idempotent, density matrices provide pairs of maximally overlapping corresponding orbitals. These optimized overlaps determine the eigenvalues and eigenfunctions of the density-difference matrices. For changes in electronic structure that accompany detachment or attachment of a single electron, the eigenfunction of the density-difference matrix with a unit eigenvalue is proportional to a Dyson orbital and equals a corresponding orbital with no non-vanishing overlaps with other corresponding orbitals. The remaining pairs of density-difference-matrix eigenfunctions are Löwdin-orthogonalized combinations of overlapping corresponding orbitals that describe the effects of orbital relaxation. Probability factors and Fukui functions also are determined by the corresponding-orbital overlaps. The Δ SCF method changes the results of Koopmans's identity by allowing: relaxation of orbitals in final states, Dyson orbitals with non-unit probability factors, negative spin densities and negative values of Fukui functions. Both levels of theory incorrectly produce unit changes in occupation numbers of Dyson orbitals between initial and final states. The natural ionization or excitation occupation numbers provide qualitative indices of how many holes and particles pertain to a given transition. Qualitative distinctions between primary (Koopmans-like) and correlation (i.e. shake-up) states in photoelectron spectra or between singly and doubly excited states can be made with these data. Ordinary versus charge-transfer transitions may be distinguished by the degree of spatial separation between natural excitation orbitals. The present proofs of the unit and paired eigenvalues that follow from diagonalization of the difference of two, idempotent matrices are similar in approach to proofs that pertain to sums of two, idempotent matrices. The latter demonstrations confirm the conclusions of Amos and Hall that provided justification for the concept of corresponding orbitals.

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Data Availability Statement

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

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Appendix

During this investigation, a related theorem also was proven.

Theorem 5

Under the same assumptions and with the same definitions as in Theorem 1, let

$$M_4 = \begin{pmatrix} I_p & T \\ T^\dagger & -I_q \end{pmatrix}. \quad (65)$$

Then:

- (a) -1 is an eigenvalue of M_4 with multiplicity ℓ , provided that $\ell > 0$. In particular, if $\ell = q$, then $T = 0$; thus the only eigenvalues of M_4 in this case are -1 with multiplicity q , and 1 with multiplicity p .
- (b) 0 is not an eigenvalue of M_4 .
- (c) $-\sqrt{2}$ and $\sqrt{2}$ are eigenvalues of M_4 with multiplicity δ , provided that $\delta > 0$. In particular, if $\delta = q$, then the only eigenvalues of M_4 are 1 with multiplicity $p - q$, and $-\sqrt{2}$ and $\sqrt{2}$, each with multiplicity q .
- (d) 1 is an eigenvalue of M_4 with multiplicity $p - q + \ell$, provided that $p > q$ or $\ell > 0$.
- (e) All eigenvalues of M_4 different from $-1, 1, -\sqrt{2}$ and $\sqrt{2}$, if any, are of the form $\pm(1 + s_r^2)^{1/2}$, $r = 1, \dots, q - (\ell + \delta)$, where the s_r are those $|t_{j,j}|$ that are not equal to 0 or 1 .
- (f) All eigenvalues of M_4 different from $-1, 1, -\sqrt{2}$ and $\sqrt{2}$ have multiplicities not exceeding $q - \ell$. If $-\sqrt{2}$ and $\sqrt{2}$ are eigenvalues of M_4 then they both have the same multiplicity, which may not exceed q . If -1 is an eigenvalue of M_4 its multiplicity may not exceed q . If 1 is an eigenvalue of M_4 , its multiplicity may not exceed p .

Proof:

Assume that $T \neq 0$ and define

$$E_4 = \begin{pmatrix} I_p & T \\ 0 & (\lambda - 1)I_q \end{pmatrix} \quad (66)$$

and $F_4 = (\lambda I_n - M_4)E_4$. Then

$$\det(F_4) = (\lambda - 1)^q \det(\lambda I_n - M_4). \quad (67)$$

But

$$F_4 = \begin{pmatrix} (\lambda - 1)I_p & 0 \\ -T^\dagger & (\lambda^2 - 1)I_q - T^\dagger T \end{pmatrix}. \quad (68)$$

Therefore, we also have

$$\det(F_4) = (\lambda - 1)^p \det((\lambda^2 - 1)I_q - T^\dagger T). \quad (69)$$

Since the entries $d_{i,j}$ of the $q \times q$ matrix $T^\dagger T$ are such that $d_{i,j} = 0$ if $i \neq j$ and $d_{j,j} = |t_{j,j}|^2$, $j = 1, \dots, q$, we conclude that

$$(\lambda^2 - 1)I_q - T^\dagger T = \text{diag}((\lambda^2 - 1) - |t_{j,j}|^2). \quad (70)$$

Thus

$$\det(F_4) = (\lambda - 1)^p \prod_{j=1}^q (\lambda^2 - 1 - |t_{j,j}|^2), \quad (71)$$

and from equation 67 we deduce that

$$\begin{aligned} \det(\lambda I_n - M_4) &= (\lambda - 1)^{p-q} \prod_{j=1}^q (\lambda^2 - 1 - |t_{j,j}|^2) \\ &= (\lambda - 1)^{p-q+\ell} (\lambda + 1)^\ell (\lambda - \sqrt{2})^\delta (\lambda + \sqrt{2})^\delta \prod_{j=1}^{q-(\ell+\delta)} (\lambda^2 - 1 - s_r^2), \quad (72) \end{aligned}$$

where the s_r are those $|t_{j,j}|$ that are not equal to 0 or 1. If $\delta = q$, then $p - q + 2\ell + 2\delta = n + 2\ell$; thus $\ell = 0$. To prove that the multiplicity of 1 may not exceed p note that $\ell \leq q$; thus $p - q + \ell \leq p$.

□

Table 1: Eigenvalues of $\mathbf{P} + \mathbf{Q}$ and Their Multiplicities

Eigenvalue	1	0	2	$1 + t_{rr}$	$1 - t_{rr}$
Multiplicity	$p - q + 2\ell$	$m - p - q + \delta$	δ	$q - \ell - \delta$	$q - \ell - \delta$

Table 2: Eigenvalues of $\mathbf{P} - \mathbf{Q}$ and Their Multiplicities

Eigenvalue	1	-1	0	$+\sqrt{1-t_{rr}^2}$	$-\sqrt{1-t_{rr}^2}$
Multiplicity	$p - q + \ell$	ℓ	$m - p - q + 2\delta$	$q - \ell - \delta$	$q - \ell - \delta$

Table 3: Approximate and exact Dyson orbitals, probability factors and changes in occupation numbers

Theory	Dyson Orbital	Probability Factor	Δn_{Dyson}^a	$\Delta n_{non-Dyson}^a$
Koopmans	ψ	1	± 1	0
Δ SCF	$\sqrt{P}\phi^b$	$0 \leq P \leq 1$	± 1	$0 \leq \Delta n_{non-Dyson} \leq 1$
Diagonal Σ	$\sqrt{P}\psi$	$0 \leq P \leq 1$	$0 \leq \Delta n_{Dyson} \leq 1$	$0 \leq \Delta n_{non-Dyson} \leq 1$
Exact	$\sum_r^{all} c_r \psi_r$	$0 \leq P \leq 1$	$0 \leq \Delta n_{Dyson} \leq 1$	$0 \leq \Delta n_{non-Dyson} \leq 1$

^a Changes in occupation number for spin-orbital $p = \Delta \langle p^\dagger p \rangle$.

^b ϕ may be expressed as a linear combination of canonical, Hartree-Fock orbitals (ψ) using equations 30 and 31.