Generalised Nonorthogonal Matrix Elements: Unifying Wick’s Theorem and the Slater–Condon Rules

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Evaluating matrix elements between nonorthogonal Slater determinants represents a key component in several modern electronic structure methods. One approach, the first-quantised generalised Slater–Condon rules, is applicable to any pair of determinants with mutually nonorthogonal orbitals, but involves biorthogonalising the occupied orbitals. Alternatively, the nonorthogonal Wick’s theorem allows matrix elements to be evaluated using second-quantisation, but fails if the two determinants have a zero overlap overall. In this contribution, we unify these two approaches by deriving an entirely generalised variant of the nonorthogonal Wick’s theorem that is applicable to pairs of determinants with both nonorthogonal orbitals and a total zero overlap. Our approach is therefore applicable to any pair of nonorthogonal Slater determinants, and can be used to evaluate matrix elements between excited configurations while only biorthogonalising the occupied orbitals in the reference determinants.

1. INTRODUCTION

Matrix elements between nonorthogonal Slater determinants are becoming increasingly common in modern electronic structure theory. For example, linear combinations of nonorthogonal Slater determinants provide the core of nonorthogonal configuration interaction (NOCI) or projected Hartree–Fock methods for capturing static correlation, while the combination of geminal-based nonorthogonal functions is an area of ongoing research. Furthermore, nonorthogonal matrix elements occur in inter-state coupling terms between state-specific excited states identified through methods such as excited-state mean-field theory, or the complete active space self-consistent field. Two main theories exist for evaluating matrix elements between two nonorthogonal Slater determinants. In the generalised Slater–Condon rules, biorthogonal occupied orbitals are constructed and a modified form of the Slater–Condon rules is applied depending on the number of zero-overlap orbital pairs in the biorthogonal basis. This approach is applicable to any pair of determinants, but each matrix element requires the diagonalisation of the occupied orbital overlap matrix. Meanwhile, the second-quantised nonorthogonal Wick’s theorem uses the Thouless transformation to relate the two determinants through an exponential operator, before evaluating matrix elements using modified contractions with respect to a single Fermi vacuum. However, the Thouless transformation is limited to determinants that are strictly nonorthogonal, and thus breaks down if there are any zero-overlap orbital pairs in the biorthogonal basis.

Computationally efficient nonorthogonal matrix elements become increasingly important in methods that use orthogonally-excited configurations from nonorthogonal reference determinants. For example, including post-NOCI dynamic correlation in methods such as perturbative NOCI-PT2 or nonorthogonal multireference CI, all involve overlap, one-body, or two-body coupling terms between excitations from nonorthogonal determinants. The number of nonorthogonal matrix elements therefore grows rapidly, and repeated biorthogonalisation of the occupied orbitals becomes prohibitively expensive. In principle, the nonorthogonal Wick’s theorem could allow these matrix elements to be evaluated using contractions between the biorthogonal reference orbitals but, until now, this requires the reference determinants to have a strictly non-zero overlap.

In this contribution, we derive an entirely generalised nonorthogonal form of Wick’s theorem that applies to any pair of determinants with nonorthogonal orbitals, even if the overall determinants have a zero overlap. This new framework, which we call the “Extended Nonorthogonal Wick’s Theorem”, provides the most general approach for deriving matrix elements using second-quantisation, allowing Wick’s theorem and the generalised Slater–Condon rules to be unified for the first time. Furthermore, our approach allows matrix elements between excited configurations to be evaluated using only biorthogonal occupied orbitals in the reference determinants. As a result, we expect that our approach will provide significant reductions in the computational cost for calculating large numbers of excited coupling terms.

To derive our generalised nonorthogonal matrix elements, we first extend Thouless’ theorem to the case where the two determinants have nonorthogonal orbitals, but have a zero overlap overall. We then show how this extended Thouless transformation can be combined with Wick’s theorem by introducing generalised nonorthogonal contractions between the second-quantisation operators. To illustrate the application of our theory, we show how the generalised Slater–Condon rules can be recovered for one- and two-body operators. Finally, we derive efficient coupling terms between excited configurations, and discuss the key advantages of our approach.
II. NOTATION

In what follows, we consider matrix elements between the two determinants $|w\Phi\rangle$ and $|x\Phi\rangle$. Each determinant is constructed from a bespoke set of molecular orbitals (MOs), represented in terms of the atomic spin-orbital basis functions $|\chi_\mu\rangle$ as

$$|w\phi_p\rangle = \sum_\mu |\chi_\mu\rangle wC^{\mu}_p. \tag{1}$$

Here, we employ the nonorthogonal tensor notation of Head-Gordon et al.\cite{Head-Gordon1995} We index the occupied MOs as $(i,j,k,...)$, the virtual MOs as $(a,b,c,...)$, and any general MO as $(p,q,r,...)$. We emphasise that the MOs are orthogonal within each Slater determinant, but are nonorthogonal between the different determinants.

In the second-quantisation perspective, the $N$-electron determinant $|\Phi\rangle$ is defined as

$$|\Phi\rangle = \prod_{i=1}^{N} w^{\dagger}b_i |\rangle, \tag{2}$$

where $|\rangle$ defines the physical vacuum and the molecular orbital creation and annihilation operators are given as

$$w^{\dagger}b_i = \sum_\mu a^{\dagger}_\mu wC^{\mu}_i \quad \text{and} \quad wb_i = \sum_\mu (wC^{\mu})^{\dagger}_i a_\mu. \tag{3}$$

The covariant atomic spin-orbital operators have only one non-zero anticommutator\cite{Lowdin1957}

$$[a_\mu, a_{\nu}]_+ = g_{\mu\nu}, \tag{4}$$

where $g_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle$ defines the corresponding covariant metric tensor (overlap matrix).\cite{Lowdin1957} At times, we will also consider the contravariant atomic spin-orbital operators $(a_\mu)^{\dagger}$ and $a_\mu$ with the anticommutator

$$[(a_\mu)^{\dagger}, a_\nu]_+ = g^{\mu\nu}. \tag{5}$$

Here, $g^{\mu\nu}$ is the contravariant metric tensor corresponding to the inverse covariant overlap matrix,\cite{Lowdin1957} i.e.

$$g^{\mu\nu} = (g^{-1})_{\mu\nu}. \tag{6}$$

III. EXTENDED THOULESS TRANSFORMATION

A. Conventional Thouless Transformation

The conventional form of Thouless’ theorem allows two nonorthogonal determinants to be related by an exponential operator of single excitations as\cite{Thouless1951}

$$|w\Phi\rangle = \exp(\tilde{Z}) |x\Phi\rangle \langle x\Phi|w\Phi\rangle. \tag{7}$$

To derive the single excitation operator $Z$, the occupied orbitals can be be transformed to a biorthogonal basis such that

$$\sum_{\mu\nu}(\tilde{C}^{\mu\ast})^{\dagger}_i g_{\mu\nu} w\tilde{C}^{\nu}_j = s_i \delta_{ij}. \tag{8}$$

Following this biorthogonalisation process, also known as Löwdin pairing,\cite{Lowdin1950,Lowdin1957} the transformed molecular orbital creation and annihilation operators are given as

$$w^{\dagger}\tilde{b}_i = \sum_\mu a^{\dagger}_\mu \tilde{C}^{\mu}_i \quad \text{and} \quad \tilde{b}_i = \sum_\mu (\tilde{C}^{\mu})^{\dagger}_p a_\mu. \tag{9}$$

The single excitation operator is then defined as

$$Z = \sum_{ia} x^{w}Z_{ai} x^{\dagger}_{ai} x^{\dagger}_{ai}, \tag{10}$$

with the $x^{w}Z_{ai}$ matrix elements given as

$$x^{w}Z_{ai} = \sum_{\mu\nu} (\tilde{C}^{\mu\ast})^{\dagger}_i g_{\mu\nu} (w\tilde{C}^{\nu})^{\dagger}_p \frac{1}{s_i}. \tag{11}$$

A brief derivation of this result can be found in Appendix A. However, this exponential representation relies on the strict nonorthogonality of the two determinants $|x\Phi\rangle|w\Phi\rangle \neq 0$; in other words, it is not applicable to a pair of determinants that are orthogonal but contain mutually nonorthogonal orbitals. Our first step is therefore a generalisation of the Thouless transformation to the case where $\langle x\Phi|w\Phi\rangle = 0$.

B. Introducing Zero-Overlap Orbitals

We begin in the biorthogonal basis identified through Löwdin pairing, with orbital coefficients satisfying Eq. (8). For a general pair of nonorthogonal orbitals, it is possible for orbital pairs to have a zero-overlap in the biorthogonal basis, where $s_i = 0$. Taking the case with $m$ zero overlaps between orbitals $k_1, \ldots, k_m$, we construct “reduced” determinants by removing the electrons in these zero-overlap orbitals to give

$$|x^{w}\Phi_{k_1\cdots k_m}\rangle = x^{\dagger}_{k_1} \cdots x^{\dagger}_{k_m} |x\Phi\rangle \tag{12a}$$

$$|w^{x}\Phi_{k_1\cdots k_m}\rangle = w^{\dagger}_{k_1} \cdots w^{\dagger}_{k_m} |w\Phi\rangle. \tag{12b}$$

These reduced determinants are strictly nonorthogonal with the non-zero reduced overlap defined as

$$x^{w}S = \langle x^{w}\Phi_{k_1\cdots k_m}|x^{w}\Phi_{k_1\cdots k_m}\rangle = \prod_{\{i|s_i \neq 0\}} s_i. \tag{13}$$

Therefore, the Thouless transformation can now be applied to the reduced determinants to give

$$|w^{x}\Phi_{k_1\cdots k_m}\rangle = \exp(\tilde{Z}) |x^{w}\Phi_{k_1\cdots k_m}\rangle x^{w}S. \tag{14}$$

Here, we have introduced the reduced single excitation operator $\tilde{Z}$ that only contains excitations from occupied orbitals with a non-zero overlap as

$$\tilde{Z} = \sum_{\{i|s_i \neq 0\}} \sum_{a} x^{w}Z_{ai} x^{\dagger}_{ai} x^{\dagger}_{ai}. \tag{15}$$
The full $N$-electron determinants are then related through second-quantisation as

$$
|\Psi^{w}\rangle = w^{b_{k_1}] \cdots w^{b_{k_m}]} \exp\left(\hat{Z}^{w}\right) x_{k_m}] \cdots x_{k_1}] |\Psi^{w}\rangle x_{w}^{w} S_{w}.
$$

Equation (16) can be further simplified by exploiting the commutativity relation $[\hat{Z}, x_{k}] = 0$ to shift the $\exp\left(\hat{Z}\right)$ operator to the far right-hand side, giving

$$
|\Psi^{w}\rangle = w^{b_{k_1}] \cdots w^{b_{k_m}]} x_{k_m}] \cdots x_{k_1}] x_{w}^{w} S_{w}.
$$

Next, introducing the relationship $\hat{z}_{k} = \exp(\hat{Z}) - 1$ allows Eq. (19) to be expanded as

$$
|\Psi^{w}\rangle = \prod_{\{k|s_{k}=0\}} \hat{z}_{k} \exp\left(\hat{Z}\right) x_{w}^{w} S_{w}.
$$

Expanding the product of $(\exp(\hat{Z}) - 1)$ terms then leads to a sum of exponential transformations where every combination of the zero-overlap single excitation operators $\hat{z}_{k}$ is either included or excluded with an appropriate phase factor, giving

$$
|\Psi^{w}\rangle = \sum_{n=0}^{m} (-1)^{(m-n)} \sum_{c_{n}} \exp\left(\hat{Z}^{c_{n}}\right) x_{w}^{w} S_{w}.
$$

Here, we have introduced the compound index $c_{n}$ to denote a particular combination of $n$ out of $m$ zero-overlap orbitals, while the superscript notation $\hat{Z}^{c_{n}}$ indicates which particular zero-overlap excitations are included in the corresponding operator, i.e.,

$$
\hat{Z}^{c_{n}} = \hat{Z} + \sum_{k \in c_{n}} \hat{z}_{k}.
$$

IV. EXTENDED NONORTHOGONAL WICK’S THEOREM

A. Conventional Wick’s Theorem

Efficiently deriving matrix elements using the conventional Wick’s theorem requires the introduction of contractions, defined for two creation or annihilation operators $b^{\dagger}_{p}$ and $b_{q}$ as

$$
\langle x_{p}^{p} x_{q}^{q} b_{p}^{\dagger} b_{q} = \left\{ x_{p}^{p} x_{q}^{q} b_{p}^{\dagger} b_{q} \right\} + \left\{ x_{p}^{p} x_{q}^{q} b_{p}^{\dagger} b_{q} \right\},
$$

where $\left\{ x_{p}^{p} x_{q}^{q} b_{p}^{\dagger} b_{q} \right\}$ represents a normal-ordered operator string with respect to the reference Fermi vacuum $|\Psi^{w}\rangle \cdots |\Psi^{w}\rangle$.

B. Zero-Overlap Transformed Operators

Using the extended Thouless transformation, we can now extend the nonorthogonal Wick’s theorem to derive matrix elements between any pair of determinants with mutually nonorthogonal orbitals. The matrix elements for general operators expressed in the atomic spin-orbital basis requires the evaluation of terms containing a string of creation and annihilation operators, such as $\langle b^{\dagger}_{p} a^{\dagger}_{q} b^{\dagger}_{r} a^{\dagger}_{s} |\Psi^{w}\rangle$. Applying the extended Thouless transformation leads to the linear combination

$$
\langle b^{\dagger}_{p} a^{\dagger}_{q} b^{\dagger}_{r} a^{\dagger}_{s} |\Psi^{w}\rangle = x_{w}^{w} S_{w} \times \sum_{n=0}^{m} (-1)^{(m-n)} \sum_{c_{n}} \exp\left(\hat{Z}^{c_{n}}\right) x_{w}^{w}.
$$

To evaluate each constituent matrix elements for the combinations $c_{n}$, we follow the approach described in Refs. 21 and
and introduce a similarity-transformed set of spin-orbital creation and annihilation operators as

\[
(d[c_n]^\mu)^\dagger = \exp \left( - \tilde{Z}^{c_n} \right) (a^\mu)^\dagger \exp \left( \tilde{Z}^{c_n} \right) \quad (28a)
\]

\[
d[c_n]^\mu = \exp \left( - \tilde{Z}^{c_n} \right) a^\mu \exp \left( \tilde{Z}^{c_n} \right). \quad (28b)
\]

An explicit derivation of these relationships can be found in Appendix B. Exploiting the identities

\[
\langle \tilde{\tau} \Phi | \exp \left( - \tilde{Z}^{c_n} \right) = \langle \tilde{\tau} \Phi | \quad (31)
\]

and

\[
\exp \left( \tilde{Z}^{c_n} \right) \exp \left( - \tilde{Z}^{c_n} \right) = \mathcal{I} \quad (32)
\]

then allows the constituent matrix elements within Eq. (27) to be expressed as

\[
\langle \tilde{\tau} \Phi | (d[c_n]^\mu)^\dagger (d[c_n]^\nu)^\dagger \cdots (d[c_n]^\sigma)^\dagger \cdots (d[c_n]^\tau)^\dagger \tilde{\tau} \Phi \rangle = \langle x \Phi | (d[c_n]^\mu)^\dagger (d[c_n]^\nu)^\dagger \cdots (d[c_n]^\sigma)^\dagger \cdots (d[c_n]^\tau)^\dagger \tilde{\tau} \Phi \rangle. \quad (33)
\]

C. The Fundamental Contraction

The extended Thouless transformation essentially converts the nonorthogonal matrix element with an asymmetric Fermi vacuum \( \langle \tilde{\tau} \Phi | \cdots | \tilde{\tau} \Phi \rangle \) to a transformed matrix element with respect to symmetric Fermi vacuum \( \langle \tilde{\tau} \Phi | \cdots | \tilde{\tau} \Phi \rangle \). Since the transformed operators \( (d[c_n]^\mu)^\dagger \) and \( (d[c_n]^\mu) \) are expressed purely in terms of the \( \tilde{b}_i^\dagger \) creation and \( \tilde{b}_i \) annihilation operators, with respect to the \( \langle \tilde{\tau} \Phi | \cdots | \tilde{\tau} \Phi \rangle \) vacuum, their non-zero contractions with respect to \( \langle \tilde{\tau} \Phi | \cdots | \tilde{\tau} \Phi \rangle \) can be derived by combining Eqs. (25) and (30) to give

\[
(d[c_n]^\mu)^\dagger (d[c_n]^\nu)^\dagger = x_w M^{\nu\mu} - \sum_{k \notin c_n} x_w P_{k}^{\nu\mu}, \quad (34a)
\]

\[
(d[c_n]^\mu)(d[c_n]^\nu)^\dagger = g^{\nu\mu} - x_w M^{\nu\mu} + \sum_{k \notin c_n} x_w P_{k}^{\nu\mu}. \quad (34b)
\]

These operators clearly depend on the particular combination \( c_n \) of included zero-overlap single excitation operators. Expanding the similarity transformation as

\[
\exp \left( - \tilde{Z}^{c_n} \right) a^\mu \exp \left( \tilde{Z}^{c_n} \right) = a^\mu - \tilde{Z}^{c_n} a^\mu, \quad (29a)
\]

and similarly for \( (a^\mu)^\dagger \), leads to the explicit forms

\[
(d[c_n]^\mu)^\dagger = \sum_{i} x_i \tilde{b}_i^\dagger (\tilde{C}^{\nu\mu})_{i}^\mu + \sum_{a} x_a \tilde{b}_a^\dagger \left[ (\tilde{C}^{\nu\mu})_{a}^\mu - \sum_{\mu \nu \in c_n} x_{\mu \nu} Z_{\mu \nu} (\tilde{C}^{\nu\mu})_{k}^\mu \right], \quad (30a)
\]

\[
d[c_n]^\mu = \sum_{i} (\tilde{C}^{\nu\mu})_{i}^\mu \tilde{b}_i + \sum_{a} \left[ \sum_{\mu \nu \in c_n} x_{\mu \nu} Z_{\mu \nu} \tilde{b}_a + \sum_{\mu \nu \in c_n} x_{\mu \nu} S_{\mu \nu} x_b + (\tilde{C}^{\nu\mu})_{a}^\mu \tilde{b}_a \right]. \quad (30b)
\]

Here, we have introduced the general notation

\[
x_{w} P_{k}^{\nu\mu} = (\tilde{w} C)^{\nu\mu}_{k}, \quad \langle 35a \rangle
\]

\[
x_{w} P_{k}^{\nu\mu} = \sum_{\{k\} \in c_n} x_{w} P_{k}^{\nu\mu}, \quad \langle 35b \rangle
\]

\[
x_{w} W_{\nu\mu} = \sum_{\{i, s\} \in c_n} (\tilde{w} C)^{\nu\mu}_{i}, \quad \langle 35c \rangle
\]

\[
x_{w} M^{\nu\mu} = x_{w} P^{\nu\mu} + x_{w} P^{\nu\mu} + x_{w} W^{\nu\mu}. \quad \langle 35d \rangle
\]

However, the overall matrix element \( \langle \tilde{\tau} \Phi | (a^\mu)^\dagger (a^\nu)^\dagger \cdots a^\sigma a^\tau \tilde{\tau} \Phi \rangle \) requires the derivation of contractions between the \( a^\mu \) and \( (a^\mu)^\dagger \) operators rather than the transformed \( d[c_n]^\mu \) and \( (d[c_n]^\mu)^\dagger \) operators. To show how a general string of operators can be evaluated using contractions, we first demonstrate the derivation of a one-body operator with only one contraction by considering the one-body co-density matrix element

\[
x_{w} \Gamma^{\nu\mu}_{1} = \langle \tilde{\tau} \Phi | (a^\mu)^\dagger a^\nu \tilde{\tau} \Phi \rangle. \quad \langle 36 \rangle
\]

Assuming that some form of Wick’s theorem can be derived, we expect this matrix element to be represented by the single contraction

\[
x_{w} \Gamma^{\nu\mu}_{1} = \langle \tilde{\tau} \Phi | (a^\mu)^\dagger a^\nu \tilde{\tau} \Phi \rangle. \quad \langle 37 \rangle
\]

Taking the most general case with \( m \) zero-overlap orbitals, the extended Thouless transformation leads to
\[
\langle \Phi | \left( a^\mu \right) \left( a^\nu \right) \Phi \rangle = x_w S \sum_{n=0}^{m} (-1)^{(m-n)} \sum_{c_n} \langle \Phi | \left( d[c_n]^\mu \right) \left( d[c_n]^\nu \right) \Phi \rangle = x_w S \sum_{n=0}^{m} (-1)^{(m-n)} \sum_{c_n} \left( x_w M_{\mu\nu} - \sum_{k \notin c_n} x_w P_k^{\mu\nu} \right).
\]  

(38)

Reversing the order of summation over \( k \) and \( c_n \) yields

\[
\langle \Phi | \left( a^\mu \right) \left( a^\nu \right) \Phi \rangle = x_w S \sum_{n=0}^{m} (-1)^{(m-n)} \left( x_w M_{\mu\nu} \left[ \sum_{c_n} 1 \right] - \sum_{k} x_w P_k^{\mu\nu} \left[ \sum_{c_n \notin k} 1 \right] \right).
\]

(39)

The first term in square brackets \( \left[ \sum_{c_n} 1 \right] \) can be recognised as the total number of ways to pick \( n \) orbitals from the \( m \) zero-overlap orbitals, given by \( \binom{m}{n} \). Similarly, the second term in square brackets \( \left[ \sum_{c_n \notin k} 1 \right] \) is the total number of ways to pick \( n \) orbitals from the \( m - 1 \) zero-overlap orbitals that remain when orbital \( k \) is excluded, given by \( \binom{m-1}{n} \). These combinatorial expansions allow Eq. (39) to be expressed as

\[
\langle \Phi | \left( a^\mu \right) \left( a^\nu \right) \Phi \rangle = x_w S \sum_{n=0}^{m} (-1)^{(m-n)} \binom{m}{n} x_w M_{\mu\nu} + \sum_{n=0}^{m-1} (-1)^{(m-1-n)} \binom{m-1}{n} x_w P_n^{\mu\nu}.
\]

(40)

Here, we note that there are no ways to exclude an orbital \( k \) when all zero-orbital overlaps are included in the complete combination \( c_m \). Exploiting the binomial expansion

\[
\sum_{y=0}^{y} (-1)^{(y-n)} \binom{y}{n} = (1 - 1)^y
\]

then leads to the closed-form expression

\[
\langle \Phi | \left( a^\mu \right) \left( a^\nu \right) \Phi \rangle = x_w S \left[ (1 - 1)^m x_w M_{\mu\nu} + (1 - 1)^{(m-1)} x_w P_n^{\mu\nu} \right].
\]

(42)

Clearly, the reduced overlap \( x_w S \) will be a prefactor for every matrix element between these nonorthogonal determinants. The remaining terms can then be used to define "fundamental contractions" for second-quantisation operators with respect to the asymmetric Fermi vacuum \( \langle \Phi \cdots | \Phi \rangle \). The form of these contractions depends on the number of zero-overlap orbitals \( m \) and, exploiting the identity \( (1 - 1)^y = \delta_{0y} \), we define the first fundamental contraction as

\[
\left( a^\mu \right) \left( a^\nu \right) = \begin{cases} x_w M_{\mu\nu} & m = 0, \\ x_w P_n^{\mu\nu} & m = 1, \\ 0 & m > 1. \end{cases}
\]

(43)

Similarly, the second fundamental contraction can be identified as

\[
\left( a^\mu \right)^{\dagger} \left( a^\nu \right)^{\dagger} = \begin{cases} x_w M_{\mu\nu} & m = 0, \\ x_w P_n^{\mu\nu} & m = 1, \\ 0 & m > 1. \end{cases}
\]

D. Combining Several Contractions

Next, we show how the fundamental contractions can be combined to derive matrix elements for longer products of creation and annihilation operators. As an example, consider the two-body reduced co-density matrix element, defined as

\[
x_w \Gamma_2^{\mu\nu} = \langle \Phi | \left( a^\mu \right) \left( a^\nu \right) \Phi \rangle.
\]

(45)

Applying Wick’s theorem, this matrix element should be given by the sum of the two contractions

\[
\langle \Phi | \left( a^\mu \right) \left( a^\nu \right) \Phi \rangle = \langle \Phi | \left( a^\mu \right) \left( a^\nu \right) \Phi \rangle + \langle \Phi | \left( a^\mu \right) \left( a^\nu \right) \Phi \rangle.
\]

(46)

Note that the second term in this expression carries a phase of \(-1\) from the intersection of the contraction lines, representing the fundamental parity of fermionic operators. Taking the first contraction as an example, we apply the extended Thouless transformation and the transformed contractions defined in Eq. (34) to give
\[ \langle \tau \Phi | (a^\dagger \mu) (a^\dagger \nu) a^\sigma a^\tau | w \Phi \rangle = x w \tilde{S} \sum_{n=0}^{m} (-1)^{(m-n)} \sum_{c_n} \langle \tau \Phi | (d[c_n] \mu)^\dagger (d[c_n] \nu)^\dagger d[c_n] \sigma d[c_n] \tau | \tau \Phi \rangle. \]

\[ = x w \tilde{S} \sum_{n=0}^{m} (-1)^{(m-n)} \left( x w M^{\tau \mu} - \sum_{k_1 \notin c_n} x w P^{\tau \mu}_{k_1} \right) \left( x w M^{\sigma \nu} - \sum_{k_2 \notin c_n} x w P^{\sigma \nu}_{k_2} \right). \]

Once again, note that the reduced overlap \(x w \tilde{S} \) appears as an overall prefactor. The order of summation over the \(k_1, k_2\) indices and \(c_n\) can then be swapped to give

\[ \langle \tau \Phi | (a^\dagger \mu) (a^\dagger \nu) a^\sigma a^\tau | w \Phi \rangle = x w \tilde{S} \sum_{n=0}^{m} (-1)^{(m-n)} \times \]

\[ \left( x w M^{\tau \mu} x w M^{\sigma \nu} \left[ \sum_{c_n} 1 \right] - \sum_{k} (x w M^{\tau \mu} x w P^{\sigma \nu}_{k} + x w P^{\tau \mu}_{k} x w M^{\sigma \nu}) \left[ \sum_{c_n \notin k} 1 \right] + \sum_{k_1, k_2} x w P^{\tau \mu}_{k_1} x w P^{\sigma \nu}_{k_2} \left[ \sum_{c_n \notin \{k_1, k_2\}} 1 \right] \right). \]

\[ \text{(47)} \]

The third term in square brackets \(\sum_{c_n \notin \{k_1, k_2\}} 1\) is simply the number of ways to pick \(n\) orbitals from the \(m-2\) zero-overlap orbitals that remain when orbitals \(k_1\) and \(k_2\) are removed, given by \((m-2)\). Applying the binomial expansion Eq. (41) in an analogous way to the single contraction recovers the closed form

\[ \langle \tau \Phi | (a^\dagger \mu) (a^\dagger \nu) a^\sigma a^\tau | w \Phi \rangle = x w \tilde{S} \left[ (1-1)^m (x w M^{\tau \mu} x w M^{\sigma \nu}) + (1-1)^{(m-1)} (x w M^{\tau \mu} x w P^{\sigma \nu} + x w P^{\tau \mu} x w M^{\sigma \nu}) + (1-1)^{(m-2)} (x w P^{\tau \mu} x w P^{\sigma \nu}) \right]. \]

\[ \text{(49)} \]

This fully contracted matrix element can then be simplified depending on the number of zero-overlap orbitals \(m\) as

\[ \langle \tau \Phi | (a^\dagger \mu) (a^\dagger \nu) a^\sigma a^\tau | w \Phi \rangle = \begin{cases} x w \tilde{S} (x w M^{\tau \mu} x w M^{\sigma \nu}) & m = 0, \\ x w \tilde{S} (x w M^{\tau \mu} x w P^{\sigma \nu} + x w P^{\tau \mu} x w M^{\sigma \nu}) & m = 1, \\ x w \tilde{S} (x w P^{\tau \mu} x w P^{\sigma \nu}) & m = 2, \\ 0 & m \geq 3, \end{cases} \]

\[ \text{(50)} \]

A similar expression can be derived for the second contraction

\[ \langle \tau \Phi | (a^\dagger \mu) (a^\dagger \nu) a^\sigma a^\tau | w \Phi \rangle = \begin{cases} x w \tilde{S} (x w M^{\tau \mu} x w M^{\sigma \nu}) & m = 0, \\ x w \tilde{S} (x w M^{\sigma \mu} x w P^{\tau \nu} + x w P^{\sigma \mu} x w M^{\tau \nu}) & m = 1, \\ x w \tilde{S} (x w P^{\sigma \mu} x w P^{\tau \nu}) & m = 2, \\ 0 & m \geq 3, \end{cases} \]

\[ \text{(51)} \]

which, analogously with the orthogonal case, will carry a \(-1\) phase factor from the intersection of the contraction lines. Combining these two equations, with their associated phase factors, yields the full expression for the two-body reduced co-density matrix elements as

\[ \langle \tau \Phi | (a^\dagger \mu) (a^\dagger \nu) a^\sigma a^\tau | w \Phi \rangle = \begin{cases} x w \tilde{S} (x w M^{\tau \mu} x w M^{\sigma \nu} - x w M^{\sigma \mu} x w M^{\tau \nu}) & m = 0, \\ x w \tilde{S} (x w P^{\tau \mu} x w M^{\sigma \nu} + x w M^{\tau \mu} x w P^{\sigma \nu} - x w P^{\sigma \mu} x w M^{\tau \nu} - x w M^{\sigma \mu} x w P^{\tau \nu}) & m = 1, \\ x w \tilde{S} (x w P^{\tau \mu} x w P^{\sigma \nu} - x w P^{\sigma \mu} x w P^{\tau \nu}) & m = 2, \\ 0 & m \geq 3. \end{cases} \]

\[ \text{(52)} \]

E. General Rules for Constructing Matrix Elements

To simplify the derivation of even longer operator strings, we note that the two-body matrix elements in Eq. (49) can be factorized into the product of two fundamental contractions with individual \(m_1\) and \(m_2\) values under the constraint \(m_1 + m_2 =
\[ \langle x^{\mu} | \mathbf{a}^\dagger \mathbf{a} \mathbf{a}^\dagger | x^\nu \rangle = x^{w} S \times \sum_{m_1, m_2} \left( (1 - 1)^{m_1} x^{w} M^{\tau \mu} + (1 - 1)^{m_1 - 1} x^{w} P^{\sigma \nu} \right) \left( (1 - 1)^{m_2} x^{w} M^{\sigma \nu} + (1 - 1)^{m_2 - 1} x^{w} P^{\sigma \nu} \right). \] (53)

Each \( m_k \) can only take values of 0 or 1 for the product of the contractions to be non-zero. Significantly, this factorised form for the multiple contractions creates an intuitive approach for extending Wick’s theorem for generalised nonorthogonal matrix elements:

1. Construct all fully contracted combinations of the operator product with the associated phase factors.
2. For each term, sum every possible way to distribute \( m \) zeros among the contractions such that \( \sum_i m_i = m \).
3. For every set of \( \{ m_i \} \) in each term, construct the relevant contribution as a product of fundamental contractions depending on whether each contraction has \( m_i = 0 \) or 1.
4. Multiply the final combined expression with the reduced overlap \( x^{w} S \).

Although we have only demonstrated up to two-body terms, this approach can be readily extended to more complex matrix elements. These rules and contractions therefore allow any matrix element to be evaluated with respect to the asymmetric Fermi vacuum \( \langle x^{\mu} | \ldots | x^\nu \rangle \) for nonorthogonal orbitals, regardless of whether the many-body determinants are orthogonal or not. As a result, this formulation is the most flexible form of Wick’s theorem, and reduces to the previous nonorthogonal\(^{28,21,30} \) or orthogonal\(^{29} \) variants under suitable restrictions on the MO coefficients. We refer to our approach as the “Extended Nonorthogonal Wick’s Theorem”. In the following Sections, we will show how these steps can be applied to recover the generalised Slater–Condron rules,\(^{18} \) and to derive matrix elements between excited configurations with respect to the nonorthogonal reference determinants.

V. GENERALISED SLATER–CONDON RULES

The generalised Slater–Condron rules provide a first-quantised approach for evaluating matrix elements between nonorthogonal determinants. A detailed description of these rules, their derivation, and their application, can be found in Ref. 18. However, to the best of our knowledge, the generalised Slater–Condron rules have never previously been derived though a second-quantised framework. In this Section, we will show how these rules can be recovered using the extended nonorthogonal Wick’s theorem.

A. One-Body Operators

Consider first the one-body operator

\[ \hat{f} = \sum_{\mu \nu} f_{\mu \nu} (a^\mu)^\dagger a^\nu, \] (54)

with the corresponding matrix element

\[ \langle x^{\mu} | \hat{f} | x^\nu \rangle = \sum_{\mu \nu} f_{\mu \nu} \langle x^{\mu} | (a^\mu)^\dagger a^\nu \rangle. \] (55)

Applying the extended nonorthogonal Wick’s theorem yields only one non-zero contraction to give

\[ \langle x^{\mu} | \hat{f} | x^\nu \rangle = \sum_{\mu \nu} f_{\mu \nu} \langle x^{\mu} | (a^\mu)^\dagger a^\nu \rangle. \] (56)

Substituting the fundamental contraction [Eq. (43)] and considering the possible values of \( m \) immediately yields the one-body generalised Slater–Condron rules as\(^{18} \)

\[ \langle x^{w} S \sum_{\mu \nu} f_{\mu \nu} (x^{w} W)^{\nu \mu} | x^{w} \rangle = \begin{cases} \text{no zeros,} & \text{for one-zero overlap}, \\ \text{one zero (} k \text{),} & \text{for two-zero overlap}, \\ 0 & \text{otherwise.} \end{cases} \] (57)

Here, we note that \( x^{w} M^{\nu \mu} = x^{w} W^{\nu \mu} \) when there are no zero-overlap orbitals, while \( x^{w} P^{\nu \mu} = x^{w} P_{k}^{\nu \mu} \) for one-zero overlap in orbital \( k \). The matrices \( x^{w} M \) and \( x^{w} P_{k} \) correspond respectively to the weighted and unweighted co-density matrices discussed in Ref. 1.

B. Two-Body Operators

Consider now a general two-body operator \( \hat{v} \) defined in second-quantisation as

\[ \hat{v} = \sum_{\mu \nu \tau \sigma} v_{\mu \nu \tau \sigma} (a^\mu)^\dagger (a^\nu)^\dagger a^\tau a^\sigma \] (58)

with the two-electron integrals in the spin-orbital basis defined as

\[ v_{\mu \nu \tau \sigma} = \langle \chi_\mu \chi_\nu | \hat{v} | \chi_\tau \chi_\sigma \rangle. \] (59)

The corresponding matrix element is then given by

\[ \langle x^{\mu} | \hat{v} | x^\nu \rangle = \sum_{\mu \nu \tau \sigma} v_{\mu \nu \tau \sigma} \langle x^{\mu} | (a^\mu)^\dagger (a^\nu)^\dagger a^\tau a^\sigma \rangle. \] (60)
Recognising the \( \langle \tilde{\Psi} \Phi (a^\nu)^\dagger (a^\sigma)^\dagger a^\sigma | \tilde{\Phi} \rangle \) term as the two-body reduced co-density matrix derived in Eq. (52), we immediately find

\[
\langle \tilde{\Psi} \Phi | \tilde{v} | \tilde{w} \Phi \rangle = \begin{cases} 
  xw \tilde{S} \sum_{\mu \nu \sigma \tau} v_{\mu \nu \sigma \tau} \left( xw M^\tau \mu xw M^\sigma \nu - xw M^\sigma \mu xw M^\tau \nu \right) & m = 0, \\
  xw \tilde{S} \sum_{\mu \nu \sigma \tau} v_{\mu \nu \sigma \tau} \left( xw P^\tau \mu xw M^\sigma \nu + xw M^\sigma \mu xw P^\tau \nu - xw P^\sigma \mu xw M^\tau \nu - xw M^\tau \mu xw P^\sigma \nu \right) & m = 1, \\
  xw \tilde{S} \sum_{\mu \nu \sigma \tau} v_{\mu \nu \sigma \tau} \left( xw P^\sigma \mu xw P^\tau \nu - xw P^\tau \mu xw P^\sigma \nu \right) & m = 2, \\
  0 & m \geq 3,
\end{cases}
\]

(61)

Here, note that the \( m = 1 \) terms each contain two terms with the single zero-overlap in either the first or second contraction respectively. Exploiting the symmetry \( v_{\mu \nu \sigma \tau} = v_{\nu \mu \tau \sigma} \) and the identity

\[
xw P^\sigma \mu xw P^\tau \nu - xw P^\tau \mu xw P^\sigma \nu = \sum_{k_1 \neq k_2} \left( xw P^\tau \mu_{k_1} xw P^\nu \tau_{k_2} - xw P^\nu \tau_{k_1} xw P^\tau \mu_{k_2} \right)
\]

(62)

then allows the two-body generalised Slater–Condon rules\(^{18}\) to be recovered as

\[
\langle \tilde{\Psi} \Phi | \tilde{v} | \tilde{w} \Phi \rangle = \begin{cases} 
  xw \tilde{S} \sum_{\mu \nu \sigma \tau} v_{\mu \nu \sigma \tau} \left( xw W^\tau \mu xw W^\sigma \nu - xw W^\sigma \mu xw W^\tau \nu \right) & \text{no zeros}, \\
  2 xw \tilde{S} \sum_{\mu \nu \sigma \tau} v_{\mu \nu \sigma \tau} \left( xw P^\tau \mu_{k_1} xw W^\sigma \nu - xw W^\sigma \mu xw P^\tau \nu \right) & \text{one zero (}k\text{)}, \\
  2 xw \tilde{S} \sum_{\mu \nu \sigma \tau} v_{\mu \nu \sigma \tau} \left( xw P^\mu \tau_{k_1} xw P^\nu \tau_{k_2} - xw P^\nu \tau_{k_1} xw P^\mu \tau_{k_2} \right) & \text{two zeros (}k_1, k_2\text{)}, \\
  0 & \text{otherwise}.
\end{cases}
\]

(63)

Note that, for the \( m = 1 \) case with one zero-overlap in orbital \( k \), we have exploited the identities \( xw P^\tau \mu_{k_1} xw P^\nu \tau_{k_2} = xw P^\tau \mu_{k_1} xw P^\nu \tau_{k_2} \) and \( xw P^\mu \tau_{k_1} xw P^\nu \tau_{k_2} = xw P^\mu \tau_{k_1} xw P^\nu \tau_{k_2} \) to introduce the simplification \( xw M \rightarrow xw W \).

VI. MATRIX ELEMENTS FOR EXCITED CONFIGURATIONS

While re-deriving the generalised Slater–Condon rules provides an important verification of the extended nonorthogonal Wick’s theorem, it does not provide any computational advantage over the original framework. On the contrary, the primary focus of our new framework involves deriving matrix elements between excited configurations from a pair of nonorthogonal determinants e.g., \( \{ \tilde{\Psi} \Phi, \Phi \} \). Terms of this form arise in perturbative corrections to NOCl,\(^{32-35}\) the NOCI-CIS approach for core excitations,\(^{32,33}\) and the evaluation of \( \langle S^2 \rangle \) coupling terms in NOCI expansions.\(^{5}\) Furthermore, these nonorthogonal matrix elements will be required to evaluate inter-state coupling elements between orbitally-optimised excited-state wave functions identified using excited-state mean-field theory\(^{10}\) or state-specific complete active space SCF.\(^{12}\)

Until now, evaluating these matrix elements has generally required the direct application of the generalised Slater–Condon rules to each pair of excitations, leading to significant computational costs associated with the biorthogonalisation of the excited determinants. In this Section, we show how the extended nonorthogonal Wick’s theorem allows these matrix elements to be evaluated using only biorthogonalised reference determinants. By constructing suitable intermediate matrix elements computed once for each pair of reference determinants, the cost of evaluating certain nonorthogonal matrix elements can then become independent of the number of electrons or basis functions.

A. Asymmetric Representation

Evaluating matrix elements between two excited determinants will generally require the evaluation of the asymmetric contractions \( \tilde{b}^\mu_{p} \tilde{b}^\nu_{q} \) with respect to the asymmetric Fermi vacuum \( \{ \tilde{\Psi} \Phi, \Phi \} \). Expanding the molecular orbital creation and annihilation operators using Eq. (3) yields

\[
\tilde{b}^\mu_{p} \tilde{b}^\nu_{q} = \sum_{\mu \nu \sigma \tau} (\tilde{w} C^\tau_{\sigma})_{\mu} g_{\mu \sigma} (\tilde{a}^\tau)_{\sigma} (\tilde{a}^\nu)_{\tau}, \quad (64a)
\]

\[
\tilde{b}^\tau_{p} \tilde{b}^\nu_{q} = \sum_{\mu \nu \sigma \tau} (\tilde{w} C^\tau_{\sigma})_{\mu} g_{\mu \sigma} (\tilde{a}^\tau)_{\sigma} (\tilde{a}^\nu)_{\tau}, \quad (64b)
\]

Introducing the fundamental contractions Eqs. (43) and (44) then reduces these expressions to different forms depending
with the one- and two-body operators can also be represented in terms of the original orbital basis, while the $xw P$ matrices are evaluated in the biorthogonal basis. As a result, only the reference determinants need to be biorthogonalised, and the remaining matrix elements are evaluated in terms of these screened overlap terms. Furthermore, these screened overlap elements are themselves one-body matrix elements that can be computed once and stored for a given pair of determinants, before being combined to evaluate more complicated matrix elements.

Crucially, the orbital coefficients used to evaluate these contractions do not need to be the same as those used to evaluate the $xw M$ and $xw P$ matrices. The excitations can therefore be represented in terms of the original orbital basis, while the $xw M$ and $xw P$ matrices are evaluated in the biorthogonal basis. As a result, only the reference determinants need to be biorthogonalised, and the remaining matrix elements are evaluated in terms of these screened overlap terms. Furthermore, these screened overlap elements are themselves one-body matrix elements that can be computed once and stored for a given pair of determinants, before being combined to evaluate more complicated matrix elements.

To take full advantage of these asymmetric contractions, the one- and two-body operators can also be represented in terms of one set of molecular orbitals as

$$\begin{align*}
\hat{f} &= \sum_{pq} x f_{pq} x^\dagger_{b_p} x^\dagger_{b_q} \\
\hat{v} &= \sum_{pqrs} x v_{pqrs} x^\dagger_{b_p} x^\dagger_{b_q} x^\dagger_{b_s} x_{b_r},
\end{align*}$$

where we have defined the transformed matrix elements

$$x f_{pq} = \sum_{\mu\nu} (x^* C^\mu)_{\nu} f_{\mu\nu} (x C)_{\nu},$$

$$x v_{pqrs} = \sum_{\mu\nu\sigma\tau} (x^* C^\mu)_{\nu} (x C^\sigma)_{\sigma} v_{\mu\nu\sigma\tau} (x C)^\tau_{\tau}.$$  

Evaluating nonorthogonal matrix elements through the extended nonorthogonal Wick’s theorem then proceeds using the same steps outlined in Section IV E. Note that the number of zero-overlap orbitals in these expressions corresponds to the biorthogonalised reference determinants, not the excited configurations.

In the following Sections, we will illustrate this process through a series of typical nonorthogonal matrix elements. As we shall see below, evaluating the sum of every combination of zero-overlap indices assigned to each contraction quickly leads to complicated equations. However, we can derive the general structure of a matrix element for the case with no zero-overlap orbitals $m = 0$, and then recover the forms for different values of $m$ by distributing the zero-overlap indices over each fundamental contraction. We will therefore focus on the parent equation with $m = 0$, which we refer to as the “canonical form”. Furthermore, any matrix element with more zero-overlap orbitals than the total number of contractions must be strictly zero.

### B. Overlap Terms

First, we consider the overlap element between excited determinants. The simplest overlap matrix element involves only a single excitation $\langle x\Phi|w\Phi^a \rangle$. For $m$ zero-overlap orbitals in the reference determinants, this single excitation matrix element can be readily identified using one contraction as

$$\langle x\Phi|w\Phi^a \rangle = \langle x\Phi|w\tilde{\Phi}^a \rangle = \begin{cases} 
\langle x\Phi|w\Phi^a \rangle_{ia} & m = 0, \\
\langle x\Phi|w\tilde{\Phi}^a \rangle_{ia} & m = 1, \\
0 & m > 1.
\end{cases}$$

Here, the canonical form is simply

$$\langle x\Phi|w\Phi^a \rangle = xw \tilde{S} w X_{ia},$$

and there is only one way to assign one zero-overlap orbital to the single contraction. Note that the reduced overlap between the reference determinants remains a prefactor for the overall matrix elements.

Next, the overlap of two single excitations $\langle x\Phi_i^a|w\Phi_j^b \rangle$ can be evaluated as
\[
\langle \Phi_i^w | \Phi_j^b \rangle = \langle \Phi_i^w | b_j^w b_i^w a_i^w a_j^w | \Phi_j^b \rangle + \langle \Phi_i^w | b_i^w b_j^w a_j^w a_i^w | \Phi_j^b \rangle
\]

\[
= \begin{cases} 
    x_w \tilde{S}(w_w X_{ja} + w_x X_{ji} x_w Y_{ab}) 
    & m = 0, \\
    x_w \tilde{S}(w_w X_{ja} + w_x X_{ji} x_w Y_{ab} + w_x X_{ji} x_w Y_{ab}) 
    & m = 1, \\
    x_w \tilde{S}(w_w X_{ja} + w_x X_{ji} x_w Y_{ab}) 
    & m = 2, \\
    0 
    & m > 2.
\end{cases}
\] (74)

The canonical form for this element is the \( m = 0 \) term

\[
\langle \Phi_i^w | \Phi_j^b \rangle = x_w \tilde{S}(w_w X_{ja} + w_x X_{ji} x_w Y_{ab}).
\] (75)

The \( m = 1 \) term is recovered by taking the sum of the two different ways to distribute one zero-overlap orbital to the two contractions, while there is only one way to distribute two zero-overlap orbitals for the \( m = 2 \) term.

As a third example, consider the double excitation overlap \( \langle \Phi_i^w | \Phi_j^{ab} \rangle \), which can be evaluated as

\[
\langle \Phi_i^w | \Phi_j^{ab} \rangle = \langle \Phi_i^w | b_a^w b_b^w b_j^w b_i^w | \Phi_j^{ab} \rangle
\]

\[
= \begin{cases} 
    x_w \tilde{S}(x_i w_w X_{ja} + w_x X_{i1} x_w X_{ja}) 
    & m = 0, \\
    x_w \tilde{S}(x_i w_w X_{ja} + w_x X_{i1} x_w X_{ja} + w_x X_{i1} x_w X_{ja}) 
    & m = 1, \\
    x_w \tilde{S}(x_i w_w X_{ja} + w_x X_{i1} x_w X_{ja}) 
    & m = 2, \\
    0 
    & m > 2.
\end{cases}
\] (76)

In this case, the minus sign arises from the intrinsic \(-1\) phase that results from the intersection of the contraction lines in \( \langle \Phi_i^w | b_a^w b_b^w b_j^w b_i^w | \Phi_j^{ab} \rangle \). The relevant canonical form of this matrix element is

\[
\langle \Phi_i^w | \Phi_j^{ab} \rangle = x_w \tilde{S}(w_w X_{ja} - w_x X_{ib} x_w X_{ja}),
\] (77)

from which the terms for \( m = 1 \) and \( m = 2 \) can be derived. Notably, this form of \( \langle \Phi_i^w | \Phi_j^{ab} \rangle \) has previously been derived for \( m = 0 \) in Refs. 22 and 26, but our derivation is now generalised for any number of zero-overlap orbitals.

### C. One-Body Operators

We now consider matrix elements for one-body operators of the form given in Eq. (69a). To further simplify the subsequent expressions, we can introduce intermediate matrices that account for partial contraction of the one-body operator. In particular, we introduce the partially contracted intermediate terms

\[
F_0 = \sum_{pq} x f_{pq} x X_{qp}
\] (78a)

\[
y_w [X F X]_{rs} = \sum_{pq} y_f x X_{rp} x f_{pq} x w X_{qs}
\] (78b)

\[
y_w [X F Y]_{rs} = \sum_{pq} y_f x X_{rp} x f_{pq} x w Y_{qs}
\] (78c)

\[
y_w [Y X F]_{rs} = \sum_{pq} y_f Y_{rp} x f_{pq} x w X_{qs}
\] (78d)

\[
y_w [Y F Y]_{rs} = \sum_{pq} y_f Y_{rp} x f_{pq} x w Y_{qs}
\] (78e)

Note that the individual contraction in the \( F_0 \) term, indicated by the \( X \) matrix, may correspond to a zero-overlap orbital pair, as indicated by the notation \( F_0 \). The \( y_w [X F X]_{rs} \) (and similar) terms correspond to two contractions, and can thus be assigned two zero overlap orbitals. The different possibilities of assigning these zero-overlap contractions is denoted as \( y_w [X F X]_{rs} \) or \( y_w [X F X]_{rs} \), and similarly for terms involving the \( Y \) contraction. Crucially, these intermediate values also correspond to orbital pairs, and can be precomputed once for each pair of reference determinants. As a result, the summation over the \( p, q \) indices is avoided for the subsequent evaluation of matrix elements between excited determinants.

To illustrate the application of this approach, we first take the simplest one-body matrix element \( \langle \Phi_i^w | f^a | \Phi_i^w \rangle \). For \( m \) zero-overlap orbitals in the reference determinants, this ma-
trix element can be expanded as
\[ \langle x | \hat{f} | \Phi^{a} \rangle = \sum_{pq} x f_{pq} \times \]
\[ \left( \langle x | \Phi^{a} | b_{p}^{x} b_{q}^{y} b_{a}^{w} b_{b}^{z} \rangle + \langle x | \Phi^{a} | b_{p}^{x} b_{q}^{y} b_{b}^{w} b_{a}^{z} \rangle \right). \] (79)

Using the contractions defined in Eqs. (65a) and (65b), and the intermediate terms defined in Eq. (78), the canonical form for \( m = 0 \) is given as
\[ \langle x | \hat{f} | \Phi^{a} \rangle = x w \hat{S} (F_{0}^{w w} X_{ia} + w w [XFY]_{ia}). \] (80)

If the \( F_{0}, w w X_{ia}, \) and \( w w [XFY]_{ia} \) are precomputed and stored once for the reference determinants, this subsequent cost of evaluating \( \langle x | \hat{f} | \Phi^{a} \rangle \) is independent of the number of electrons or basis functions. From this canonical form, expressions for \( m = 1 \) and 2 (or higher) can be identified as

\[ \langle x | \hat{f} | \Phi^{a} \rangle = \begin{cases} x w \hat{S} (F_{0}^{w w} X_{ia} + w w [XFY]_{ia}) & m = 0, \\ x w \hat{S} (F_{0}^{w w} X_{ia} + w w [XFY]_{ia} + F_{0}^{w w} X_{ia} + w w [XFY]_{ia}) & m = 1, \\ x w \hat{S} (F_{0}^{w w} X_{ia} + w w [XFY]_{ia}) & m = 2, \\ 0 & m > 2. \end{cases} \] (81)

Next, consider the coupling of two single excitations \( \langle x_{i}^{a} | \hat{f} | w \Phi^{b} \rangle \), corresponding to the fully contracted terms
\[ \langle x_{i}^{a} | \hat{f} | w \Phi^{b} \rangle = \sum_{pq} x f_{pq} \times \]
\[ \left( \langle x_{i}^{a} | \Phi^{b} | b_{p}^{x} b_{q}^{y} b_{a}^{w} b_{b}^{z} \rangle + \langle x_{i}^{a} | \Phi^{b} | b_{p}^{x} b_{q}^{y} b_{b}^{w} b_{a}^{z} \rangle + \langle x_{i}^{a} | \Phi^{b} | b_{p}^{x} b_{q}^{y} b_{a}^{w} b_{b}^{z} \rangle \right). \] (82)

In this case, the canonical form is given by
\[ \langle x_{i}^{a} | \hat{f} | w \Phi^{b} \rangle = x w \hat{S} \left( F_{0}^{x x} X_{ai}^{w w} X_{jb} + F_{0}^{w x} X_{ja}^{x w} Y_{ab} \right. \]
\[ + w w [XFY]_{jb}^{x x} X_{ai} + x w [YFX]_{ai}^{w w} X_{jb} + x w [XFY]_{ab}^{x w} X_{ja} - w w [XFX]_{ja}^{x w} Y_{ab} \right), \] (83)

Again, the form for \( m \) zero-overlap orbitals can be recovered as the sum of every way to distribute the zero-overlap contractions over the \( X, Y, \) or \( F_{0} \) terms in each product. We omit the explicit form of these \( m > 0 \) expressions to maintain brevity.

Finally, consider the one-body coupling of a reference determinant and a double excitation
\[ \langle x | \hat{f} | \Phi^{a} \rangle = \sum_{pq} x f_{pq} \times \]
\[ \left( \langle x | \Phi^{a} | b_{p}^{x} b_{q}^{y} b_{a}^{w} b_{b}^{z} \rangle + \langle x | \Phi^{a} | b_{p}^{x} b_{q}^{y} b_{b}^{w} b_{a}^{z} \rangle + \langle x | \Phi^{a} | b_{p}^{x} b_{q}^{y} b_{a}^{w} b_{b}^{z} \rangle \right). \] (84)

The corresponding canonical form for \( m = 0 \) is
\[ \langle x | \hat{f} | \Phi^{a} \rangle = x w \hat{S} \left( F_{0}^{w w} X_{ia}^{w w} X_{ja} - F_{0}^{w w} X_{ib}^{w w} X_{ja} \right. \]
\[ + w w [XFY]_{ja}^{w w} X_{ja} + w w [XFY]_{ia}^{w w} X_{ja} - w w [XFY]_{ja}^{w w} X_{ja} \right), \] (85)

from which expressions for \( m > 0 \) can be obtained as described above.

\section*{D. Two-body Operators}

will be convenient to define intermediate matrices in the

Finally, we consider matrix elements for two-body operators, with the general form given in Eq. (69b). Again, it
orbital basis that can be pre-computed for a given pair of nonorthogonal determinants. First, we introduce analogues of the Coulomb and exchange matrices, respectively defined as

$$x_J = \sum_{pqrs} x_{pqrs} x_{Xsq}$$
$$x_K = \sum_{pqr} x_{pqrs} x_{Xrq}.$$  (86)

Partially contracted intermediate matrices can then be defined as e.g.,

$$yw[X(J-K)X]_{rs} = \sum_{pq} y_{pq} X_{rp}(J-K)_{pq} x_{wXqs}$$  (87a)
$$yw[Y(J-K)X]_{rs} = \sum_{pq} y_{pq} Y_{rp}(J-K)_{pq} x_{wXqs}$$  (87b)
$$yw[X(J-K)Y]_{rs} = \sum_{pq} y_{pq} X_{rp}(J-K)_{pq} y_{wYqs}$$  (87c)
$$yw[Y(J-K)Y]_{rs} = \sum_{pq} y_{pq} Y_{rp}(J-K)_{pq} y_{wYqs},$$  (87d)

with the constant value

$$V_0 = \sum_{pqrs} x_{pqrs}(x_{XXsq} x_{Xrp} - x_{XXr} x_{Xsp}).$$  (88)

Like the one-body intermediate matrices, note that, when the zero-overlap orbitals are distributed among the contractions, these zeros may be independently assigned to any of the $X$, $Y$, or $(J-K)$ terms, as each of these contain one contraction. For example, with $m = 1$, one must consider the sum of three terms given as e.g.,

$$yw[X(J-K)X]_{rs} + yw[X(J-K)X]_{rs} + yw[X(J-K)X]_{rs},$$  (89)

where

$$x_J = \sum_{pq} x_{pqrs} x_{Xsq}$$  (90a)
$$x_K = \sum_{pqr} x_{pqrs} x_{Xrq}.$$  (90b)

On the contrary, the $V_0$ constant term corresponds to two contractions and can be assigned two zero-overlap orbitals. Noting the symmetry $x_{pqrs} = x_{pqsr}$, we denote these possibilities as

$$\tilde{V}_0 = \sum_{pqrs} x_{pqrs}(x_{XXsq} x_{Xrp} - x_{XXr} x_{Xsp})$$  (91a)
$$\tilde{V}_0 = \sum_{pqrs} x_{pqrs}(x_{XXsq} x_{Xrp} - x_{XXr} x_{Xsp}).$$  (91b)

To illustrate the application of this approach for excited configurations, we first consider the two-body matrix element

$$\langle x\Phi|\tilde{v}^i w\Phi_i^e\rangle = \sum_{pqrs} x_{pqrs} \times \left( \langle x\Phi|\tilde{v}^i b_q b_s b_r b_i w\Phi_i \rangle + \langle x\Phi|\tilde{v}^i b_q b_s r w b_i w\Phi_i \rangle + \langle x\Phi|\tilde{v}^i b_q b_s b_r w b_i w\Phi_i \rangle + \langle x\Phi|\tilde{v}^i b_q b_s r w b_i w\Phi_i \rangle \right).$$  (92)

Combining each contraction, and exploiting the intermediates in Eqs. (87) and (88) yields the canonical form ($m = 0$) for this matrix element as

$$\langle x\Phi|\tilde{v}^i w\Phi_i^e\rangle = x_{wv} \tilde{S}(V_0 x_{wv} x_{ia} + 2 x_{wv} X_{ia})$$  (93)

Distributing the zero-overlap orbitals among each contraction then leads to explicit expressions for all $m$ values as

$$\langle x\Phi|\tilde{v}^i w\Phi_i^e\rangle = \begin{cases} x_{wv} \tilde{S}(V_0 x_{wv} x_{ia} + 2 x_{wv} X_{ia}) & m = 0 \\ x_{wv} \tilde{S}(V_0 x_{wv} x_{ia} + 2 x_{wv} X_{ia}) & m = 1 \\ x_{wv} \tilde{S}(V_0 x_{wv} x_{ia} + 2 x_{wv} X_{ia}) & m = 2 \\ x_{wv} \tilde{S}(V_0 x_{wv} x_{ia} + 2 x_{wv} X_{ia}) & m = 3 \\ 0 & m > 3. \end{cases}$$  (94)
Next, we consider the two-body coupling of two singly excited determinants as
\[
\langle x\Phi^a_i | v | w\Phi^b_j \rangle = \sum_{pqrs} x v_{pqrs} \langle x\Phi | w^0 | wi^0 | bj^0 | ab^0 | w\Phi \rangle.
\] (95)

With a total of 24 possible ways to fully contract the corresponding matrix element, we maintain brevity by directly presenting the canonical form for \(m = 0\) as
\[
\langle x\Phi^a_1 | v | w\Phi^b_1 \rangle = x w \hat{S} \times \left[ V_0(xw)a_{xw}b_{xb} + xw x_{ij} - \frac{1}{2} \sum_{pqrs} x v_{pqrs} x_{pqrs} a_{xw}b_{xb} - \frac{1}{2} \sum_{pqrs} x v_{pqrs} x_{pqrs} a_{xw}b_{xb} \right].
\] (96)

From here, expressions for the cases with \(m > 0\) can be recovered by distributing the zero-overlap orbitals over the contractions associated with the \(V, X, (J-K)\), or \(Y\) matrices. While partially contracted intermediate expressions could also be evaluated to avoid the nested summation on the last line in Eq. (96), this will generally incur an unacceptably large storage cost.

Finally, we consider the two-body coupling of a reference determinant and a double excitation
\[
\langle x\Phi | v | w\Phi^{ab}_ij \rangle = \sum_{pqrs} x v_{pqrs} \langle x\Phi | w^0 | i^0 | j^0 | ab^0 | w\Phi \rangle.
\] (97)

Again, there are a total of 24 possible ways to fully contract the corresponding matrix element, so we advance directly to the canonical form for \(m = 0\), given as
\[
\langle x\Phi | v | w\Phi^{ab}_ij \rangle = x w \hat{S} \times \left[ V_0(xw)a_{xw}b_{xb} - xw x_{ia} - \frac{1}{2} \sum_{pqrs} x v_{pqrs} x_{pqrs} a_{xw}b_{xb} - \frac{1}{2} \sum_{pqrs} x v_{pqrs} x_{pqrs} a_{xw}b_{xb} \right].
\] (98)

We note that this formula has previously been identified in Ref. 26 for \(m = 0\), but our approach now allows this result to be extended for \(m > 0\).

VII. CONCLUDING REMARKS

Intuitive derivations and efficient implementations of nonorthogonal matrix elements are becoming increasingly important for the development of nonorthogonal configuration interaction methods and inter-state coupling terms for state-specific excited state wave functions. However, until now, the evaluation of these matrix elements has relied on the generalised Slater–Condon rules, while the second-quantised nonorthogonal Wick’s theorem fails when there are any zero-overlap orbital pairs between the reference determinants. In this work, we have extended the nonorthogonal Wick’s theorem to the case where the two determinants have nonorthogonal orbitals, but have a zero many-electron overlap. This new theory, which we call the Extended Nonorthogonal Wick’s theorem, provides the most generalised framework for evaluating matrix elements between two nonorthogonal determinants using second quantisation.

To illustrate the application of the Extended Nonorthogonal Wick’s theorem, we have provided the first derivation of the generalised Slater–Condon rules using second-quantisation. We have also derived typical matrix elements between excited configurations from a nonorthogonal pair of reference determinants. For overlap terms and one-body operators, these excited nonorthogonal matrix elements can be expressed in terms of one-body intermediate terms that can be precomputed and stored for a given pair of reference determinants. As a result, the subsequent cost of evaluating the coupling of excited configurations is independent of the number of electrons or basis functions. This feature will lead to a significant reduction in the cost of evaluating large numbers of nonorthogonal matrix elements compared to a naive application of the generalised Slater–Condon rules, and we will demonstrate this speed-up using particular examples in future publications. Ultimately, we believe that our generalised framework for nonorthogonal matrix elements will accelerate and encourage further developments in nonorthogonal methods across electronic structure theory.
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Appendix A: Thouless’ Theorem

Thouless’ Theorem\textsuperscript{19} allows any Slater determinant to be represented using only single excitations from another determinant, i.e.

\begin{equation}
|w\Phi\rangle = \exp(Z)|\bar{x}\Phi\rangle. \tag{A1}
\end{equation}

Here, we follow Ref. \textsuperscript{31} and provide a brief derivation of this theorem. First, the two sets of second-quantisation operators can be related as

\begin{equation}
w_{ij} = \sum_j x_{ij} A_{ji} + \sum_b x_{ib} B_{bi}, \tag{A2a}
\end{equation}

\begin{equation}
= \sum_j x_{ij} \bar{B}_{ja} + \sum_b x_{ib} D_{ba}, \tag{A2b}
\end{equation}

where

\begin{equation}
w_{i} = \sum_{j} x_{ij} A_{ji}, \tag{A3a}
\end{equation}

\begin{equation}
= \sum_{j} x_{ij} \bar{B}_{ja}, \tag{A3b}
\end{equation}

\begin{equation}
w_{i} = \sum_{j} x_{ij} B_{ja} \tag{A3c}
\end{equation}

\begin{equation}
= \sum_{j} x_{ij} D_{ba}. \tag{A3d}
\end{equation}

are sub-blocks of the orbital overlap matrix. Taking a suitable transformation among the orbitals of \(|\Phi_w\rangle\) allows these to be further reduced to

\begin{equation}
w_{i} = x_{i} + \sum_j x_{ij} B_{aj} (x_{j} A_{ji}), \tag{A4a}
\end{equation}

\begin{equation}
= \sum_j x_{ij} \bar{B}_{ja}, \tag{A4b}
\end{equation}

The occupied orbitals can then be represented by the transformation

\begin{equation}
w_{i} = x_{i} + \sum_a x_{ia} \bar{B}_{aj} w_{a}. \tag{A5}
\end{equation}

where now

\begin{equation}
w_{i} = \sum_{j} x_{ij} B_{aj} (x_{j} A_{ji}). \tag{A6}
\end{equation}

Finally, if the occupied orbitals are represented in a biorthogonal basis satisfying Eq. (8), then the \(Z\) matrix elements are given simply as

\begin{equation}
x_{w} Z_{ai} = \sum_{\mu} \langle \bar{z}^{\alpha \\ C^*}_{\mu} |_{i} | g_{\mu} \nu (w \bar{C})_{\nu}^{\mu} \right|_{i} \frac{1}{\delta}. \tag{A8}
\end{equation}

Appendix B: Similarity Transformed Operators

To evaluate common matrix elements using the single excitation operators defined in Eq. (22), we consider the similarity transformed operators

\begin{equation}
(d[c_{n}]^\mu)^\dagger = \exp\left(-\hat{Z}^c_n\right)(a^\mu)^\dagger \exp\left(\hat{Z}^c_n\right) \tag{B1a}
\end{equation}

\begin{equation}
(d[c_{n}]^\mu) = \exp\left(-\hat{Z}^c_n\right)(a^\mu) \exp\left(\hat{Z}^c_n\right). \tag{B1b}
\end{equation}

First, consider the expansion of \((d[c_{n}]^\mu)^\dagger\) as

\begin{equation}
(d[c_{n}]^\mu)^\dagger = \exp\left(-\hat{Z}^c_n\right)(a^\mu)^\dagger \exp\left(\hat{Z}^c_n\right) \tag{B2}
\end{equation}

Noting the commutation relation

\begin{equation}
[x_{w} B_{ai}, x_{w} B_{aj}] = x_{w} B_{ai} \delta_{ij}, \tag{B3}
\end{equation}

and expanding \((a^\mu)^\dagger\) in terms of the \(x_{w} B_{ai}\) operators with Eq. (22) leads to

\begin{equation}
(d[c_{n}]^\mu)^\dagger = \sum_{p} \sum_{\mu} x_{w} B_{ai} \langle \bar{z}^{\alpha \\ C^*}_{\mu} |_{p} \tag{B4}
\end{equation}

Finally, separating the summation over \(p\) into a summation over the occupied orbitals \(i\) and the virtual orbitals \(a\) recovers the form given in Eq. (30a). Applying a similar approach for the \((d[c_{n}]^\mu)\) operators then recovers the expression in Eq. (30b).

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