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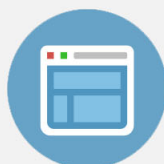
A tensor formulation of many-electron theory in a nonorthogonal single-particle basis

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We apply tensor methods to formulate theories of electron correlation in nonorthogonal basis sets. The resulting equations are manifestly invariant to nonorthogonal basis transformations, between functions spanning either the occupied or virtual subspaces of the one-particle Hilbert space. The tensor approach is readily employed in either first or second quantization. As examples, second-order Møller–Plesset perturbation theory, and coupled cluster theory with single and double substitutions, including noniterative triples, are recast using the tensor formalism. This gives equations which are invariant to larger classes of transformations than existing expressions. Procedures for truncating these equations are discussed. © *1998 American Institute of Physics.* [S0021-9606(98)02702-0]

I. INTRODUCTION

We present a formulation of many-electron theory which can be readily applied to problems involving nonorthogonal single-particle basis sets. By contrast, standard treatments[1–3] of many-body methods in electronic structure theory, be they first quantization based or second quantization based, implicitly depend upon an underlying orthonormal single-particle basis. The main reason for employing orthogonal representations is that they are widely believed to be simpler. However, we shall show that with the tensor notation, it is possible to obtain expressions that are general to nonorthogonal basis sets with little additional complication.

The first purpose of allowing nonorthogonal functions is to obtain expressions for many-electron theories that are as general as possible. Given such equations, new and useful practical approximations may arise. For example, recent advances in linear scaling methods[4,5] for mean field electronic structure calculations depend critically on the use of localized nonorthogonal functions. Analogous functions provide a natural representation in which the description of electron correlation via many-body theories can be cast in local terms. A spatially localized treatment of electron correlation[6,7] is one way to reduce the unphysical scaling of computational cost with molecular size that afflicts orthogonal basis formulations of many-body theories.

The usual approach[2,6,7] to obtaining electronic structure equations in a nonorthogonal basis is to explicitly carry the metric (overlap) matrices. Such equations are substantially more cumbersome than in the usual orthogonal representation. The alternative we pursue is based on the fact that electronic structure equations are usually operator relations, which are merely represented in a given basis. The operators depend only on the vector space spanned by the basis functions, rather than details of the basis functions such as nonorthogonality. Their matrix representations are second (or higher) rank tensors. Employing tensor calculus[8–11] ensures

all equations are properly invariant to linear transformations of the basis. This point has only rarely been emphasized in quantum chemistry.[12]

In Sec. II, we review the treatment of the one-particle basis using tensor analysis. This is an application of standard tensor methods to quantum mechanics in a finite-dimensional one-particle Hilbert space. While tensor analysis usually assumes real variables, quantum mechanics requires us to employ complex variables. The generalization necessary to achieve this is relatively slight, and has been discussed in other contexts previously.[12–14] We emphasize projectively partitioning the one particle space into occupied and virtual subspaces. The related problem of exact linear dependence in the one-particle basis is treated in the Appendix.

The many-body problem is discussed in Sec. III, as an application of tensor theory. Some second quantization treatments allow nonorthogonal functions,[15–17] although they are not tensor based. Also some correlation methods have made partial use of nonorthogonal expansion spaces to achieve important advantages.[6,7] However, to our knowledge, tensor techniques have not been employed to treat the many-electron problem previously. In first quantization, generalizations of Slater's rules for matrix elements are obtained, while in second quantization, Wick's theorem holds, and lead to representations of one- and two-particle operators in terms of the quasiparticle reference.

In Sec. IV we obtain defining equations for several popular many-body theories in a nonorthogonal representation. We treat second-order Møller–Plesset theory (MP2),[18] and coupled cluster theory with single and double substitutions (CCSD),[19] including noniterative triples.[20] This connects with existing equations which have made partial use of nonorthogonality for MP2[6,21–24] and CCSD,[25] although the present equations are more general. As such they lead to interesting possibilities for new ''local'' correlation methods, which we begin to explore elsewhere.[26] We discuss general issues associated with truncating the tensor equations in Sec. V.

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II. SINGLE-PARTICLE EXPANSION SPACES

We assume a one-particle basis set (e.g., atomic orbitals), of finite dimension, N, which we denote as $\{|\phi_\mu\rangle\}$, using Dirac's bra-ket notation.[27] These functions may be complex. The fact that any observable in quantum mechanics is invariant to linear transformations of this underlying basis is the motivation for adopting the tools of tensor analysis.[8,9] A tensor (like a scalar or a vector) may be represented in terms of a coordinate system, or a basis expansion, but is invariant to transformations of the basis functions spanning this space. Tensor algebra has been employed previously for one-electron tight-binding and self-consistent field problems for this reason.[12,14,28]

Briefly, subscript indices denote *covariant* quantities, which transform on a change of coordinates in the same way that the basis vectors themselves do. Superscripts denote *contravariant* quantities which transform in the opposite (inverse) way. The *rank* of a tensor is its number of indices: scalars, vectors, and matrices are tensors of rank 0, 1, and 2, respectively. A tensor of rank $p+q$ with p covariant and q contravariant indices is denoted as (p,q). The order of tensor indices is usually important, and is carried by placeholders ($\cdot$) if the tensor is of mixed covariant and contravariant character. The *addition* of two tensors is valid (yields another tensor) only if both tensors have the same number of covariant and contravariant indices. The *tensor product* of tensors of rank p and q is a tensor of rank $p+q$. If the same symbol appears as both a covariant and contravariant index, then summation is implied (Einstein convention). The result of such a summation is invariant to coordinate changes because of the inverse sense in which covariant and contravariant quantities transform, and is termed a *contraction*.

The given single-particle basis defines a set of (complex) covariant basis kets, with an overlap (or metric) matrix $S_{\mu\nu} = \langle\phi_\mu|\phi_\nu\rangle$, which is a covariant tensor of second rank. To allow the basis kets to be complex, *we adopt the convention that the first index of a second-rank tensor of matrix elements is to be identified with a bra, while the second index is to be identified with a ket*. Hence the order of the two indices matters. Complex conjugation reverses their positions: $(S_{\mu\nu})^* = S_{\nu\mu}$. The inverse of the overlap matrix is a contravariant tensor (since the trace of its product with the covariant overlap matrix is a scalar, N, which is the basis dimension).

Covariant and contravariant *metric tensors* are overlap and inverse overlap matrices:

$$g_{\mu\nu} \equiv S_{\mu\nu}, \tag{1}$$

$$g^{\mu\nu} \equiv (S^{-1})_{\mu\nu}. \tag{2}$$

They convert covariant indices to contravariant and vice versa because contravariant basis vectors are *defined* by the action of the contravariant metric tensor on the regular basis vectors. Hence the covariant basis functions are recovered from the contravariant basis vectors by using the covariant metric tensor. Thus

$$\langle\phi^\mu| = g^{\mu\nu}\langle\phi_\nu|, \tag{3}$$

$$|\phi_\mu\rangle = |\phi^\nu\rangle g_{\nu\mu}, \tag{4}$$

$$\langle\phi^\mu|\phi_\nu\rangle = \delta^\mu_{\cdot\nu}, \tag{5}$$

$$\langle\phi^\mu|\phi^\nu\rangle = g^{\mu\nu}. \tag{6}$$

From Eq. (5), the contravariant basis bras are biorthogonal to the covariant basis kets. Equation (6) shows that the contravariant metric tensor is the overlap matrix of the contravariant basis vectors. The adjoint operation (†) is conveniently defined as mapping numbers into complex conjugates, bras into kets, reversing order, *and turning covariant indices into contravariant and vice versa*.

With the above definitions we can compactly define the form of a projection operator onto this space, as well as general one- and two-electron operators:

$$\hat{I} = |\phi_\mu\rangle\langle\phi^\mu|, \tag{7}$$

$$\hat{F} = |\phi_\mu\rangle F^\mu_{\cdot\nu}\langle\phi^\nu|, \tag{8}$$

$$\hat{G} = |\phi_\mu(1)\rangle|\phi_\nu(2)\rangle\langle\phi^\mu\phi^\nu|\phi_\lambda\phi_\sigma\rangle\langle\phi^\sigma(2)|\langle\phi^\lambda(1)|. \tag{9}$$

Pairing of covariant and contravariant indices implies overall invariance of the operators to basis transformations. The placeholder in Eq. (8) reminds us that the first index is associated with a (contravariant) bra, while the second index is a (covariant) ket: $F^\mu_{\cdot\nu} \equiv \langle\phi^\mu|\hat{F}|\phi_\nu\rangle$. **F** is not a Hermitian matrix in this representation, although $\hat{F}$ is Hermitian. Note that in an orthogonal basis, the distinction between covariant and contravariant vanishes because the metric is the unit matrix, and the expressions are standard.

The above equations associate covariant indices with kets and contravariant indices with bras, which is the *natural* or proper representation.[13,29] We employ it preferentially because it yields maximal correspondence between nonorthogonal and orthogonal representations (metric tensors do not appear). Using metric tensors to alter the character of indices, we can write three other forms for each of Eqs. (7) and (8), and 15 other forms for Eq. (9). *In all tensors we list indices associated with bras first, followed by indices associated with kets*. With this convention, contractions over a repeated index will generally involve one member of the pair being bra-type, and one ket-type (in addition to one being covariant and the other contravariant).

As a simple example, consider a one-particle density operator $\hat{P}$ that commutes with a one-electron Hamiltonian:

$$\hat{F}\hat{P} - \hat{P}\hat{F} = 0. \tag{10}$$

Introducing the natural representations [from Eq. (8) for example] for both $\hat{P}$ and $\hat{F}$ gives an equation that is faithful to the operator algebra of Eq. (10):

$$F^\mu_{\cdot\lambda}P^\lambda_{\cdot\nu} - P^\mu_{\cdot\lambda}F^\lambda_{\cdot\nu} = 0. \tag{11}$$

We can convert to the usual fully covariant form, by use of the metric matrices, including premultiplying by the covariant metric tensor [Eq. (1)]:

$$F_{\mu\lambda}P^{\lambda\sigma}g_{\sigma\nu} - g_{\mu\lambda}P^{\lambda\sigma}F_{\sigma\nu} = 0. \tag{12}$$

This representation is not directly isomorphic with the operator equation, and so is less ''natural.''

To summarize, in standard nontensorial treatments of one-electron problems in nonorthogonal basis sets, one *implicitly* adopts particular conventions for the matrix representations of operators. The tensor character of the resulting matrices is then unclear, and it is all too easy to violate the rules for tensor addition and contraction (as emphasized in Ref. 28). Likewise it is unclear whether equations transform correctly under a change of basis. By contrast, the power and the simplicity of tensor notation is that the properties of operator matrices are made *explicit* via the covariant and contravariant character of the indices.

Many-electron theory usually depends upon a partitioning of the one-particle Hilbert space into two subspaces. One consists of levels which are occupied in a reference configuration, and the other consists of unoccupied (virtual) functions. Thus we can write:

$$\hat{I} = \hat{P} + \hat{Q}, \tag{13}$$

where the operators $\hat{I}$, $\hat{P}$, and $\hat{Q}$ are projectors (as defined by idempotency, $\hat{P}^2 = \hat{P}$, $\hat{Q}^2 = \hat{Q}$) onto the full space and the occupied and virtual subspaces, respectively. $\hat{P}$ is usually obtained from the mean-field Hartree–Fock problem, similar to Eqs. (10)–(12), subject to idempotency and given total electron number. From Eq. (13), all functions which lie entirely within the occupied space are orthogonal to functions lying entirely in the virtual space. This applies to any mix of covariant and contravariant basis vectors, and is a condition of *strong orthogonality*.

Henceforth, we consider transformations of the single-particle basis within the occupied or virtual subspaces separately, rather than within the full space. Most approximate many-electron theories are invariant only to this restricted class of transformations (which leaves $\hat{P}$ and $\hat{Q}$ invariant). Indices $i,j,k,\dots$ denote functions spanning the occupied subspace, indices $a,b,c,\dots$ denote functions spanning the virtual subspace, and indices $\mu,\nu,\lambda,\sigma,\dots$ denote functions lying in the full one-particle space.

One choice for the occupied and virtual functions are the orthogonal levels that diagonalize the mean-field Hartree–Fock Hamiltonian, $\hat{F}$. Electron correlation equations are sometimes presented *specifically* in this canonical basis, and are hence not invariant to any change of basis. More general ''noncanonical'' orthogonal functions are sometimes used, such as in gradient theory,[30] or with localized orbitals. However, the most general choice are functions that are *nonorthogonal* within the occupied and virtual subspaces. A simple example of such functions are *projected atomic orbitals* for the occupied and virtual subspaces, as defined by acting with the projectors $\hat{P}$ and $\hat{Q}$ on the parent set of atomic orbitals. These functions are considered in the Appendix, as part of the issue of treating linear dependence within the one particle space.

III. MANY-PARTICLE SYSTEMS

A. Covariant *n*-electron determinants

We assume a single-particle basis of dimension N, partitioned as in Eq. (13) into occupied and virtual subspaces (dimension n and $N-n$), each spanned by linearly independent functions (as discussed in the Appendix, linear dependence poses no practical problem either). The simplest many-electron wave function is a single determinant $|\Phi\rangle$, comprised of the n covariant functions spanning $\hat{P}$. We call $|\Phi\rangle$ the *covariant reference ket*:

$$|\Phi\rangle = (n!)^{-1/2}\det(|\phi_1\rangle|\phi_2\rangle\cdots|\phi_i\rangle\cdots|\phi_n\rangle). \tag{14}$$

What is the tensor character of $|\Phi\rangle$? This follows from how $|\Phi\rangle$ transforms under nonorthogonal transformations of the underlying single-particle basis functions spanning either $\hat{P}$ or $\hat{Q}$. Since $|\Phi\rangle$ depends on tensor products of n single-particle functions, it is an nth rank antisymmetric tensor. The properties of antisymmetric tensors are well known[10,11] as part of exterior algebra or Grassman algebra. An important fact is that if the dimension of the underlying single particle basis is S, then the dimension of the subspace of nth rank tensors which are antisymmetric is ${}^SC_n$. This is 1 if $S=n$, as is the case for $|\Phi\rangle$ under transformations of the occupied space, or ${}^{N-n}C_0$ for the virtual space. This permits substantial simplification, because a basis function spanning a one-dimensional subspace behaves much like a scalar under transformation of the basis.

In fact, a nonsingular linear transformation, $\mathbf{C}$, of the one-electron kets spanning the occupied space only alters the covariant reference ket by a constant, $\det(\mathbf{C})$. The proof is based on rewriting Eq. (14) as $|\Phi\rangle = (n!)^{-1/2}\det(\Theta)$, where Θ is a matrix whose rows are electron labels, and whose columns are occupied covariant orbital labels. Under transformation with $\mathbf{C}$:

$$(n!)^{1/2}|\Phi\rangle' = \det(\Theta')$$
$$= \det(\Theta\mathbf{C}) = \det(\Theta)\det(\mathbf{C}) = |\Phi\rangle\det(\mathbf{C}). \tag{15}$$

An antisymmetric nth rank tensor which transforms this way is a *relative tensor* of rank 0 and weight 1 (or a pseudoscalar). Hence we can focus only on (the small number of) single-particle levels that are altered from their configuration (occupied or not) in the reference by the correlation treatment, rather than treating substituted determinants as general nth rank tensors. The weight 1 refers to occupied basis transformations, while the tensor is of weight 0 with respect to virtual basis transformations, as is trivially proven.

Many electron expansion spaces are generated by replacing covariant occupied levels by covariant virtual levels. The set of all single substitutions of occupied levels, i, by virtual levels a, the corresponding set of all double substitutions, etc., comprise well-defined subspaces of the full n-electron Hilbert space, $\mathbf{H}_n$ (which consists of all substitutions through n-fold).

$$\mathbf{H}_n = 0 \oplus S \oplus D \oplus T \oplus \cdots \oplus n. \tag{16}$$

In general, electron correlation techniques seek an approximate solution of the Schrödinger equation that is defined only within such subspaces. For example, a trial wave function that depends on single and double substitutions can be completely determined by solving a Schrödinger-like equation within the $0 \oplus S \oplus D$ subspace.

We state the tensor properties of the substituted determinants that span these many-electron S, D, T subspaces, under transformations of the occupied and virtual single-particle basis sets without proof. A covariant virtual level a, introduced by substitution, transforms covariantly. The hole index, i, of an occupied level that has been substituted, transforms contravariantly, consistent with creating a hole by projection with a biorthogonal contravariant bra orbital. These nth rank antisymmetric tensors are also relative tensors, of rank (m,m), for m-fold substitutions, with weight 1 for occupied basis transformations, and weight 0 for virtual basis transformations. A single substitution of an occupied (covariant) level i by a virtual (covariant) level a is written as $|\Phi_{\bullet a}^{\ i}\rangle$, while double substitutions are $|\Phi_{\bullet\bullet ab}^{\ ij}\rangle$.

The space spanned by any given level of substitutions of occupied levels by virtuals is closed under nonsingular linear transformations of occupied and/or virtual levels. This follows directly from the fact that strong orthogonality between occupied and virtual subspaces is preserved under nonunitary (nonsingular) transformations of the one-particle basis set within the occupied and virtual subspaces. To give a concrete example, single substitutions are not mixed with double substitutions under transformations of this type. Note that subsets of these spaces are generally not closed under linear transformations.

The tensor character of substitution amplitudes is opposite to the many-electron basis vectors so that their contractions are properly invariant to transformations of the basis. Operators which generate invariant mixtures of substituted determinants can then be written as

$$\hat{T}_1|\Phi\rangle = t_{\bullet i}^{\ a}|\Phi_{\bullet a}^{\ i}\rangle, \tag{17}$$

$$\hat{T}_2|\Phi\rangle = \tfrac{1}{4} t_{\bullet\bullet ij}^{\ ab}|\Phi_{\bullet\bullet ab}^{\ ij}\rangle. \tag{18}$$

The amplitude tensors can be transformed from this natural representation with metric matrices in order to alter the character of the indices if desired.

B. Projection equations

We define many-electron dual spaces, which preserve the biorthogonality present between contravariant and covariant single-particle levels, starting from a determinant of contravariant bras, which is the n-electron *contravariant reference bra*:

$$\langle\Phi| = (n!)^{-1/2} \det(\langle\phi^1|\langle\phi^2|\cdots\langle\phi^i|\cdots\langle\phi^n|) \tag{19}$$

There are corresponding manifolds of substituted bras, $\{\langle\Phi_{\bullet i}^{a}|\}$, $\{\langle\Phi_{\bullet\bullet ij}^{ab}|\}$, etc. *In the dual space, the tensor character of indices is reversed: occupied indices (holes) are covariant, virtual indices (particles) are contravariant. For example, we replace occupied level $\langle\phi^i|$ with virtual level $\langle\phi^a|$*

in the single substitution $\langle\Phi_{\bullet i}^{a}|$. These are all relative tensors of weight -1 for occupied basis transformations, because by construction they transform in a reciprocal way to the relative tensors of Sec. III A. They are the adjoints of the corresponding covariant many-electron kets.

Solution of Schrödinger-like equations in the many-electron subspace spanned by a given level of substituted determinants can be achieved by forming projection equations with the appropriate dual vectors. Biorthogonal representations arise in unsymmetric eigenvalue problems, such as coupled cluster excited state methods.[31] They are also sometimes employed in valence bond methods.[32] In our case, the projection equations are components of an absolute tensor which represents the many-electron equations in a subspace. It is invariant to transformations of the underlying basis, provided the projections are complete within each given substituted manifold (i.e., all double substitutions, for example).

Matrix elements of operators between many-electron bras and kets in the natural representation are slight generalizations of Slater's rules[2] for the orthogonal case, with all new information contained within the covariant and contravariant character of the indices. The key to this close analogy is the natural representation in which covariant and contravariant character is consistently reversed between many-electron kets and bras. This is a tremendous contrast relative to the complexity of matrix elements between determinants of nonorthogonal functions in both bra and ket, which do not have the biorthogonality property (e.g., expressions in Ref. 2).

For the identity operator (overlaps), as a result of orthonormality of functions in the dual space with functions in normal (covariant) basis, only diagonal overlaps are nonzero. Thus:

$$\langle\Phi|\Phi\rangle = 1, \tag{20a}$$

$$\langle\Phi_{\bullet j}^{b}|\Phi_{\bullet a}^{i}\rangle = \delta_j^i \delta_a^b, \tag{20b}$$

$$\langle\Phi_{\bullet\bullet kl}^{cd}|\Phi_{\bullet\bullet ab}^{ij}\rangle = (\delta_k^i \delta_l^j - \delta_l^i \delta_k^j)(\delta_a^c \delta_b^d - \delta_a^d \delta_b^c) = \delta_{kl}^{ij} \delta_{ab}^{cd}. \tag{20c}$$

In Eq. (20c), we have simplified the final expression by introducing the generalized Kronecker delta[10,11] (whose definition is obvious from the full equation).

For one-electron operators, we derive results whose form is also familiar,[1] as a direct result of the biorthogonality between many-electron basis kets and the dual basis bras:

$$\langle\Phi|F|\Phi\rangle = F_{\bullet i}^{\ i} = g^{ij}F_{ji}, \tag{21a}$$

$$\langle\Phi_{\bullet i}^{a}|F|\Phi\rangle = F_{\bullet i}^{\ a} = g^{ab}F_{bi}, \tag{21b}$$

We next consider two-electron operators. The tensor analog of the antisymmetrized ("double bar") two-electron integrals is a fourth-rank tensor that in the natural representation has two covariant (ket) indices and two contravariant (bra) indices,

$$\mathbb{I}_{\bullet\bullet rs}^{pq} = \langle\phi^p\phi^q|\phi_r\phi_s\rangle - \langle\phi^p\phi^q|\phi_s\phi_r\rangle. \tag{22}$$

This appears in matrix elements of the two-electron repulsion operator:

$$\langle \Phi | G | \Phi \rangle = \tfrac{1}{2} \mathbb{I}^{ij}_{\bullet\bullet ij} = \tfrac{1}{2} g^{ik} g^{jl} \mathbb{I}_{klij}, \tag{23a}$$

$$\langle \Phi^a_{\bullet i} | G | \Phi \rangle = \mathbb{I}^{aj}_{\bullet\bullet ij} = g^{ab} g^{ik} \mathbb{I}_{bkij}, \tag{23b}$$

$$\langle \Phi^{ab}_{\bullet\bullet ij} | G | \Phi \rangle = \mathbb{I}^{ab}_{\bullet\bullet ij} = g^{ac} g^{bd} \mathbb{I}_{cdij}. \tag{23c}$$

In addition to the natural representation, we have employed the metric tensors to express the results in terms of fully covariant two-electron integrals.

C. Second quantization with the quasiparticle reference

Second quantization in nonorthogonal basis sets has been presented previously,[13,15–17] with Ref. 15 being particularly definitive. We shall use the natural representation for this section, to make the notation as transparent as possible. Of course, tensor character can always be altered if necessary by the covariant and contravariant metric matrices. Due to our focus on the many-particle problem, it is not convenient to define creation and destruction operators with respect to the zero particle vacuum, unlike some previous work on nonorthogonal basis sets.[13]

We take the so-called quasiparticle (QP) vacuum as our reference:[2,3] a single determinant of n occupied functions. In the natural representation, the covariant reference ket contains the occupied set of covariant basis vectors, while the contravariant reference bra contains the set of occupied contravariant functions. *Thus for substituted many-electron kets, particles (levels outside the QP reference which become filled) are covariant in character while holes (levels within the QP reference which become vacated) are contravariant. In the dual space of substituted many-electron bras, particles are contravariant while holes are covariant.* All QP creation and destruction operators defined below obey this simple convention.

We must distinguish operations on virtual functions (which can create or destroy particles in the QP vacuum) from operations on occupied functions (which will create or destroy holes in the QP vacuum). For the particle operators in the virtual space in the natural representation:

$a^\dagger_a \equiv$ QP *particle creation operator for* $|\phi_a\rangle$

     $\equiv$ QP *destruction operator for* $\langle \phi^a |,$

$a^b \equiv$ QP *particle destruction operator for* $|\phi_b\rangle$

     $\equiv$ QP *creation operator for* $\langle \phi^b |,$

The anticommutation relations for the particle operators follow by any of the usual derivations as:

$$\{a^a, a^\dagger_b\} = \delta^a_b, \tag{24a}$$

$$\{a^\dagger_a, a^\dagger_b\} = \{a^a, a^b\} = 0. \tag{24b}$$

All differences relative to the usual orthogonal basis treatments are contained in the covariant and contravariant character of the indices. If we were not in the natural representation, we would find overlaps for the anticommutator in Eq.

(24a). In a redundant representation (see Appendix), the idempotent matrix of overlaps of covariant and contravariant levels replaces the Kronecker delta:

$$\{a^a, a^\dagger_b\} = g^a_{\bullet b}. \tag{24c}$$

For functions spanning the occupied space, the identity of creation and destruction operators reverses, as we create and destroy holes in the QP vacuum:

$a^i \equiv$ QP *hole creation operator for* $|\phi_i\rangle$

     $\equiv$ QP *hole destruction operator for* $\langle \phi^i |,$

$a^\dagger_i \equiv$ QP *hole destruction operator for* $|\phi_i\rangle$

     $\equiv$ QP *hole creation operator for* $\langle \phi^i |,$

The anticommutation relations are:

$$\{a^i, a^\dagger_j\} = \delta^i_j, \tag{25a}$$

$$\{a^\dagger_i, a^\dagger_j\} = \{a^i, a^j\} = 0. \tag{25b}$$

Due to strong orthogonality between levels in the occupied and virtual one-particle spaces, all anticommutators between particle and hole operators are zero, as in the orthogonal basis. In a redundant representation, $g^i_{\bullet j}$ replaces δ^i_j in Eq. (25a), analogous to how Eq. (24c) generalizes Eq. (24a).

Contraction is central to evaluating matrix elements within second quantization. The contraction of operators x_1 and x_2 is defined as the difference between their product, and their QP normal ordered product. The normal ordered string has particle–hole creation operators to the left, and destruction operators to the right, multiplied by the parity of the permutation necessary to take the product to normal order. Thus:

$$\overset{\frown}{x_1 x_2} = x_1 x_2 - N[x_1 x_2] = \langle \Phi | x_1 x_2 | \Phi \rangle \tag{26}$$

Based on the anticommutation relations above, the only nonzero contractions between any pair of particle-hole creation and destruction operators are:

$$\overset{\frown}{a^a a^\dagger_b} = \delta^a_b \tag{27a}$$

$$\overset{\frown}{a^\dagger_i a^j} = \delta^j_i \tag{27b}$$

To evaluate many-electron operator matrix elements, we apply Wick's theorem (e.g., Ref. 2 for orthogonal basis sets), which expresses a string of creation and destruction operators of length m, as a terminating sum of partial contractions of the string in normal order:

$$x_1 x_2 \cdots x_m = N[x_1 x_2 \cdots x_m] + \sum N[\overline{x_1 x_2} \cdots x_m] + \sum N[\overline{x_1 x_2} \overline{\cdots x_m}]$$

$$+ \cdots + \sum_{m/2\text{-fold contractions}} N[\overline{x_1 x_2} \overline{x_3 \cdots x_m}^{\circ\circ\circ}] \tag{28}$$

Since vacuum expectation values of normal-ordered operator strings are zero, the vacuum expectation value involves only the fully contracted terms. Again, apart from the newly explicit tensor character of the operators, these results are identical with the familiar orthogonal basis case. Relative to previous treatments of many-electron theory involving nonorthogonal single particle expansion spaces, this is the real value of the present approach.

Using either Wick's theorem directly, or from inspection of the orthogonal basis results, we can now obtain general expressions for one and two-electron operators:

$$\hat{H} = H^i_{\bullet i} + H^p_{\bullet q} N[a^\dagger_p a^q], \tag{29}$$

$$\hat{G} = \tfrac{1}{2} \mathbb{I}^{ij}_{\bullet\bullet ij} + \mathbb{I}^{pi}_{\bullet\bullet qi} N[a^\dagger_p a^q] + \tfrac{1}{4} \mathbb{I}^{pq}_{\bullet\bullet rs} N[a^\dagger_p a^\dagger_q a^s a^r]. \tag{30}$$

In these expressions, indices $i,j,k..$ are occupied levels, and p,q,r,s are general levels where the indices run over both occupied and virtual ranges, and the antisymmetrized two-electron integrals were defined in Eq. (22). These second quantization tools are sufficient to reduce n-electron matrix elements to mixtures of 1- and 2-electron matrix elements, as for the generalized Slater's rules given in Sec. III (B), or the correlation methods treated in Sec. IV.

IV. EXAMPLES OF ELECTRON CORRELATION TECHNIQUES IN NONORTHOGONAL BASIS SETS

A. Second-order Møller–Plesset perturbation theory

Second-order Møller–Plesset perturbation theory[18] (MP2) is the simplest useful wave-function-based treatment of electron-correlation effects.[33] MP2 usually uses canonical orbitals which make the Fock operator diagonal in the many-electron basis. ''Noncanonical'' MP2 theory is invariant to unitary transformations within the occupied and virtual spaces and was introduced in the context of the local MP2 method,[6,21,22] and gradient theory.[34] The former also uses nonorthogonal functions to span the virtual function space. We obtain equations which are invariant to nonunitary transformations within both the occupied and virtual spaces.

The MP2 equations follow from a partition of the Hamiltonian in the form:

$$\hat{H} = \hat{F}^{(0)} + \lambda \hat{V}^{(1)}, \tag{31}$$

$$\hat{F}^{(0)} = F^i_{\bullet i} + F^a_{\bullet b} N[a^\dagger_a a^b] - F^i_{\bullet j} N[a^j a^\dagger_i]. \tag{32}$$

We exclude occupied-virtual elements of the Fock operator from Eq. (32), so that the single reference is an eigenket of $\hat{F}^{(0)}$.[35] They are included in the fluctuation potential:

$$\hat{V} = -\tfrac{1}{2} \mathbb{I}^{ij}_{\bullet\bullet ij} + F^i_{\bullet a} N[a^\dagger_i a^a] + F^a_{\bullet i} N[a^\dagger_a a^i]$$
$$+ \tfrac{1}{4} \mathbb{I}^{pq}_{\bullet\bullet rs} N[a^\dagger_p a^\dagger_q a^s a^r]. \tag{33}$$

Second-order perturbation theory is then the leading correlation correction to the reference energy.

There is a delightful isomorphism between our new treatment and existing noncanonical orthogonal basis equations.[34] The first-order equation for the perturbed wave function is resolved by projection with singly and doubly substituted bra determinants (in the dual basis) to yield equations for the first-order single and double substitution amplitudes:

$$\langle \Phi^a_{\bullet i} | \hat{F}^{(0)} | \hat{T}^{(1)}_1 \Phi \rangle + \langle \Phi^a_{\bullet i} | \hat{V}^{(1)} | \Phi \rangle = 0, \tag{34a}$$

$$\langle \Phi^{ab}_{\bullet\bullet ij} | \hat{F}^{(0)} | \hat{T}^{(1)}_2 \Phi \rangle + \langle \Phi^{ab}_{\bullet\bullet ij} | \hat{V}^{(1)} | \Phi \rangle = 0. \tag{34b}$$

These equations may be written out in explicit spin–orbital notation as

$$F^a_{\bullet b} t^b_{\bullet i} - F^j_{\bullet i} t^a_{\bullet j} + F^a_{\bullet i} = 0, \tag{35a}$$

$$F^b_{\bullet c} t^{ac}_{\bullet\bullet ij} + F^a_{\bullet c} t^{cb}_{\bullet\bullet ij} - F^k_{\bullet j} t^{ab}_{\bullet\bullet ik} - F^k_{\bullet i} t^{ab}_{\bullet\bullet kj} + \mathbb{I}^{ab}_{\bullet\bullet ij} = 0. \tag{35b}$$

The MP2 energy is obtained from the second-order expansion of the eigenvalue equation followed by projection with the bra determinant:

$$E^{(2)} = \langle \Phi | \hat{V}^{(1)} | (\hat{T}^{(1)}_1 + \hat{T}^{(1)}_2) \Phi \rangle = F^i_{\bullet a} t^a_{\bullet i} + \tfrac{1}{4} \mathbb{I}^{ij}_{\bullet\bullet ab} t^{ab}_{\bullet\bullet ij}. \tag{36}$$

Equations (35) and (36) are the most general form of the MP2 equations yet presented: invariant to nonunitary linear transformations within both the occupied and virtual subspaces, and redundant (linearly dependent) representations. To specialize to the canonical case, take an orthogonal basis (in which case the covariant–contravariant distinction vanishes) satisfying the Brillouin theorem (such that first-order singles are zero), and diagonalize the occupied–occupied and virtual–virtual blocks of the Fock matrix (so that the doubles equations uncouple).

We can relate our MP2 equations to those presented for a redundant nonorthogonal virtual representation, and a noncanonical orthogonal occupied basis.[6,21,23] We convert to the fully covariant representation for one- and two-electron matrix elements via metric matrices:

$$\{[F_{ac}g_{bd}+g_{ac}F_{bd}]g_{ik}g_{jl}-g_{ac}g_{bd}[F_{ik}g_{jl}+g_{ik}F_{jl}]\}t^{klcd}$$

$$=-\mathbb{I}_{ijab}, \tag{37a}$$

$$E^{(2)}=\tfrac{1}{4}\mathbb{I}_{abij}t^{ijab}. \tag{37b}$$

These equations generalize the starting point for the Pulay–Saebø local MP2 method.[6,23,24] In their method, occupied indices are orthogonal, so that the distinction between covariant and contravariant occupied indices vanishes. Also, for real basis functions, $\mathbb{I}_{abij}=(\mathbb{I}_{ijab})^*=\mathbb{I}_{ijab}$.

B. Coupled cluster theory limited to single and double substitutions

We consider coupled cluster theory[36] truncated at single and double substitutions (CCSD). CCSD was definitively treated within an orthogonal spinorbital formalism by Purvis and Bartlett,[19] and many subsequent formulations have been presented. However, none has allowed general orbital nonorthogonality. A strong isomorphism with the conventional orthogonal formulation will again be evident. In fact, given knowledge of the many-electron natural representations, the nonorthogonal equations can be inferred from the orthogonal basis work! By contrast, previous equations[25] which are nonorthogonal in just the virtual space shows no such direct isomorphism, due to explicitly carrying the metric matrices in the equations.

The variables in the CCSD method (energy, single and double substitution amplitudes) are determined by satisfying the energy eigenvalue problem in the subspace spanned by the reference bra and the corresponding singly and doubly substituted bras:

$$\langle\Phi|\hat{H}-E|\exp(\hat{T}_1+\hat{T}_2)\Phi\rangle=0, \tag{38a}$$

$$\langle\Phi^a_{\bullet i}|\hat{H}-E|\exp(\hat{T}_1+\hat{T}_2)\Phi\rangle=0, \tag{38b}$$

$$\langle\Phi^{ab}_{\bullet\bullet ij}|\hat{H}-E|\exp(\hat{T}_1+\hat{T}_2)\Phi\rangle=0. \tag{38c}$$

The translation of these many-electron operator equations into spin–orbital expressions involving only one- and two-electron matrix elements leads to the following expression for the energy:

$$E=E_0+F^i_{\bullet a}t^a_{\bullet i}+\tfrac{1}{4}\mathbb{I}^{ij}_{\bullet\bullet ab}(t^{ab}_{\bullet\bullet ij}+t^a_{\bullet i}t^b_{\bullet j}-t^a_{\bullet j}t^b_{\bullet i}). \tag{39}$$

where $E_0=\langle\Phi|\hat{H}|\Phi\rangle=F^i_{\bullet i}-\tfrac{1}{2}\mathbb{I}^{ij}_{\bullet\bullet ij}$. The singles equations become

$$F^a_{\bullet i}+F^a_{\bullet b}t^b_{\bullet i}-F^j_{\bullet i}t^a_{\bullet j}+\mathbb{I}^{aj}_{\bullet\bullet ib}t^b_{\bullet j}+(t^{ba}_{\bullet\bullet ji}-t^b_{\bullet i}t^a_{\bullet j})F^j_{\bullet b}$$

$$+\tfrac{1}{2}\mathbb{I}^{ja}_{\bullet\bullet bc}(t^{bc}_{\bullet\bullet ji}+t^b_{\bullet j}t^c_{\bullet i}-t^b_{\bullet i}t^c_{\bullet j})-\tfrac{1}{2}\mathbb{I}^{jk}_{\bullet\bullet bi}(t^{ba}_{\bullet\bullet jk}+t^b_{\bullet j}t^a_{\bullet k}-t^b_{\bullet k}t^a_{\bullet j})$$

$$-\tfrac{1}{2}\mathbb{I}^{jk}_{\bullet\bullet cb}t^c_{\bullet i}t^{ab}_{\bullet\bullet jk}-\tfrac{1}{2}\mathbb{I}^{jk}_{\bullet\bullet bc}t^a_{\bullet k}t^{bc}_{\bullet\bullet ji}-\mathbb{I}^{jk}_{\bullet\bullet cb}t^c_{\bullet k}(t^{ab}_{\bullet\bullet ij}-t^a_{\bullet i}t^b_{\bullet j})=0, \tag{40}$$

while the more involved equations for the doubles are:

$$\hat{A}_2\{\mathbb{I}^{ab}_{\bullet\bullet ij}+2F^b_{\bullet c}t^{ac}_{\bullet\bullet ij}-2F^k_{\bullet j}t^{ab}_{\bullet\bullet ik}-2\mathbb{I}^{ak}_{\bullet\bullet ij}t^b_{\bullet k}+2\mathbb{I}^{ab}_{\bullet\bullet cj}t^c_{\bullet i}$$

$$+\tfrac{1}{2}\mathbb{I}^{ab}_{\bullet\bullet cd}C^{cd}_{\bullet\bullet ij}+\tfrac{1}{2}\,\mathbb{I}^{kl}_{\bullet\bullet ij}C^{ab}_{\bullet\bullet kl}-4\mathbb{I}^{bk}_{\bullet\bullet jc}\widetilde{C}^{ac}_{\bullet\bullet ki}-2F^k_{\bullet c}t^a_{\bullet k}t^{cb}_{\bullet\bullet ij}$$

$$-2F^k_{\bullet c}t^c_{\bullet i}t^{ab}_{\bullet\bullet kj}+2t^d_{\bullet k}\mathbb{I}^{bk}_{\bullet\bullet cd}t^{ac}_{\bullet\bullet ij}-2t^c_{\bullet l}\mathbb{I}^{lk}_{\bullet\bullet cj}t^{ab}_{\bullet\bullet ik}+2\alpha^{ab}_{\bullet\bullet cj}t^c_{\bullet i}$$

$$+2\alpha^{kb}_{\bullet\bullet ij}t^a_{\bullet k}+\tfrac{1}{4}\mathbb{I}^{kl}_{\bullet\bullet cd}[C^{cd}_{\bullet\bullet ij}C^{ab}_{\bullet\bullet kl}-4t^{ac}_{\bullet\bullet ij}C^{bd}_{\bullet\bullet kl}-4t^{ab}_{\bullet\bullet ik}C^{cd}_{\bullet\bullet jl}$$

$$+8\widetilde{C}^{ac}_{\bullet\bullet ki}\widetilde{C}^{bd}_{\bullet\bullet lj}-8t^d_{\bullet i}t^b_{\bullet k}t^a_{\bullet l}t^c_{\bullet j}]\}=0. \tag{41}$$

Here the operator $\hat{A}_2$ is the antisymmetrizer for a doubles array, which is defined by its action on a fourth-rank tensor involving two occupied and two virtual indices as

$$\hat{A}_2\{w^{ab}_{\bullet\bullet ij}\}=\tfrac{1}{4}[w^{ab}_{\bullet\bullet ij}-w^{ab}_{\bullet\bullet ji}-w^{ba}_{\bullet\bullet ij}+w^{ba}_{\bullet\bullet ji}]. \tag{42}$$

We have defined our intermediates to match the definitions given by Purvis and Bartlett,[19] to make the correspondence with an orthogonal formulation as clear as possible:

$$C^{ab}_{\bullet\bullet ij}=t^{ab}_{\bullet\bullet ij}+t^a_{\bullet i}t^b_{\bullet j}-t^a_{\bullet j}t^b_{\bullet i}=\widetilde{C}^{ab}_{\bullet\bullet ij}-t^a_{\bullet j}t^b_{\bullet i}, \tag{43}$$

$$B^{ab}_{\bullet\bullet ij}=t^{ab}_{\bullet\bullet ij}+\tfrac{1}{3}t^a_{\bullet i}t^b_{\bullet j}-\tfrac{1}{3}t^a_{\bullet j}t^b_{\bullet i}=\widetilde{B}^{ab}_{\bullet\bullet ij}-\tfrac{1}{3}t^a_{\bullet j}t^b_{\bullet i}, \tag{44}$$

$$\alpha^{kb}_{\bullet\bullet ij}=\mathbb{I}^{kl}_{\bullet\bullet cj}\widetilde{B}^{cb}_{\bullet\bullet il}-\mathbb{I}^{kl}_{\bullet\bullet ci}\widetilde{B}^{cb}_{\bullet\bullet jl}-\tfrac{1}{2}\mathbb{I}^{kb}_{\bullet\bullet cd}B^{cd}_{\bullet\bullet ij}, \tag{45}$$

$$\alpha^{ab}_{\bullet\bullet cj}=\mathbb{I}^{bk}_{\bullet\bullet cd}\widetilde{B}^{ad}_{\bullet\bullet kj}-\mathbb{I}^{ak}_{\bullet\bullet cd}\widetilde{B}^{bd}_{\bullet\bullet kj}-\tfrac{1}{2}\mathbb{I}^{kl}_{\bullet\bullet jc}B^{ab}_{\bullet\bullet kl}. \tag{46}$$

In the natural representation, the algebra is isomorphic to the familiar orthogonal basis case, although the character of indices can be altered between covariant and contravariant via metric matrices. Other algebraic formulations of the CCSD equations[37] in orthogonal basis sets may also be conveniently generalized to nonorthogonal representations in the same way.

C. Noniterative CCSD(T) triples correction to CCSD

The most widely used approximation to the electron correlation energy which includes triple substitutions is the CCSD(T) correction to CCSD.[20] The Brillouin theorem is assumed to be satisfied, and the CCSD(T) triples amplitudes are obtained from an approximation to the CCSDT equations, motivated by perturbation theory.[38] Only the contribution from doubles is included, (which is leading order in Møller–Plesset perturbation theory), and the zero-order Hamiltonian is used for the triples–triples block:

$$\langle\Phi^{abc}_{\bullet\bullet\bullet ijk}|\hat{F}|\hat{T}_3\Phi\rangle+\langle\Phi^{abc}_{\bullet\bullet\bullet ijk}|\hat{V}|\hat{T}_2\Phi\rangle=0. \tag{47}$$

The $\hat{T}_2$ operator contains the (known) CCSD doubles amplitudes, and the $\hat{T}_3$ amplitudes are to be solved for. In terms of nonorthogonal occupied and virtual spin orbitals, these equations become:

$$\hat{A}_3\{3F^c_{\bullet d}t^{abd}_{\bullet\bullet\bullet ijk}-3F^l_{\bullet k}t^{abc}_{\bullet\bullet\bullet ijl}\}+\bar{\bar{\nu}}^{abc}_{\bullet\bullet\bullet ijk}=0, \tag{48}$$

where $\hat{A}_3$ is an antisymmetrizer for a triples array [akin to Eq. (42) for $\hat{A}_2$], and the array defining the right-hand side of these linear equations is

$$\bar{\bar{\nu}}^{abc}_{\bullet\bullet\bullet ijk}=\hat{A}_3\{9t^{ad}_{\bullet\bullet ij}\mathbb{I}^{bc}_{\bullet\bullet dk}+9t^{ab}_{\bullet\bullet il}\mathbb{I}^{cl}_{\bullet\bullet jk}\}. \tag{49}$$

In the canonical orthogonal basis, $\mathbf{F}$ is diagonal, and thus the triples amplitudes are uncoupled.

The CCSD(T) correction to the CCSD energy is then defined as follows:

$$\delta E_{\text{CCSD(T)}} = \langle (\hat{T}_1 + \hat{T}_2)\Phi | \hat{V} | T_3 \Phi \rangle$$
$$= \tfrac{1}{36}(\bar{\nu}_{\bullet\bullet\bullet abc}^{ijk} + \bar{\bar{\nu}}_{\bullet\bullet\bullet abc}^{ijk}) t_{\bullet\bullet\bullet ijk}^{abc}, \tag{50}$$

where the doubles term, $\bar{\bar{\nu}}_{\bullet\bullet\bullet abc}^{ijk}$, is the adjoint of Eq. (49):

$$\bar{\bar{\nu}}_{\bullet\bullet\bullet abc}^{ijk} = (\bar{\nu}_{\bullet\bullet\bullet ijk}^{abc})^{\dagger} \equiv \hat{A}_3\{9t_{\bullet\bullet ad}^{ij}\mathbb{I}_{\bullet\bullet bc}^{dk} + 9t_{\bullet\bullet ab}^{il}\mathbb{I}_{\bullet\bullet cl}^{jk}\}, \tag{51}$$

while the singles term is the adjoint of

$$\bar{\nu}_{\bullet\bullet\bullet ijk}^{abc} = \hat{A}_3\{-9t_{\bullet i}^{a}\mathbb{I}_{\bullet\bullet jk}^{bc}\}. \tag{52}$$

These equations generalize CCSD(T) to nonorthogonal occupied and virtual representations.

V. TRUNCATIONS OF THE MP2 ELECTRON CORRELATION EQUATIONS

We have reexpressed electron correlation methods so that nonorthogonal sets of functions can be used to span both occupied and virtual subspaces, and these representations can contain exact linear dependencies. This may yield new methods for truncating the equations based on spatial locality of the functions. Here we give some comments on making truncations in a manner which retains invariance to classes of basis transformation which are as broad as possible. We consider the MP2 equations as the simplest concrete example.

Let us initially make the two-electron integrals in the fully covariant representation, $\mathbb{I}_{ijab}$

(1) Definition of the truncated four-index ket space. We discard integrals based on a local criterion, such as the magnitude of $\mathbb{I}_{ijab}$ being below a numerical threshold.[39] We are left with a reduced set in which the indices a,b,i,j are no longer independent. Instead the retained $abij$ define a single (compound) linear index, $(abij)$. In tensor terms, this truncation has reduced the rank of the four index space from 4 to 1. We surround the compound index with brackets to indicate that the individual indices are no longer independent.

(2) The definition of the metric of the truncated four-index space. Having made the doubles indices a,b,i,j dependent, we can no longer define the dual four index space in terms of products of the inverses of the single index metrics. Defining the dual space of truncated bra functions in that manner would mean that the correlation equations are not solved in a well-defined subspace. Instead we first define the metric associated with our truncated ket space. This takes the form:

$$G_{(ijab)(klcd)} = g_{ik}g_{jl}g_{ac}g_{bd}. \tag{53}$$

If we need to transform a truncated tensor of character $t_{(ijab)}$ into character $t^{(klcd)}$, then the metric, (53), must be inverted either implicitly or explicitly:

$$G^{(klcd)(ijab)}t_{(ijab)} = t^{(klcd)}. \tag{54}$$

(3) Solution of the truncated equations. We wish to solve the tensor MP2 equations within the subspace selected in step (1) above, with metric characterized in step (2). This leads us to the following set of truncated equations, in terms of the set of truncated amplitudes:

$$\{[F_{ac}g_{bd} + g_{ac}F_{bd}]g_{ik}g_{il} - g_{ac}g_{bd}[F_{ik}g_{jl} + g_{ik}F_{jl}]\}t^{(klcd)}$$
$$= -\mathbb{I}_{(ijab)}. \tag{55}$$

This set of equations explicitly defines the form of the coefficient matrix in the truncated 4-index space. In general such equations are solved by iterative techniques, such as conjugate gradients or DIIS.[40] However, the residual on each iteration (left-hand side minus right-hand side) is not tensorially consistent with the form of the amplitudes that we must update. Conversion is accomplished via solution of Eq. (54) (which need not be exact for this purpose). Finally, given the converged amplitudes, we obtain the (local) MP2 energy in the form:

$$E^{(2)} = \tfrac{1}{4}t^{(ijab)}\mathbb{I}_{(ijab)}. \tag{56}$$

This achieves solution of the equations within a well-defined subspace of the full set of double excitations. *Hence a truncated method of this type is rigorously invariant to linear transformations that mix the retained excitations.* However, it is not invariant to general transformations of the occupied and virtual functions, because the selection of double excitations to retain was made using a particular set of occupied and virtual basis functions.

Such a truncation is most general, in that we assume all four retained indices are related, by contrast with the untruncated equations, in which the four indices are all independent. A less general possibility is to introduce a local truncation which couples together only pairs of indices (one occupied and one virtual index). This has the advantage of retaining direct product structure in the metric, and the coefficient matrix. Thus the metric in the truncated doubles space is the direct product of metrics associated with truncated second-rank tensors:

$$G_{(ia)(jb)(kc)(ld)} = G_{(ia)(kc)}G_{(jb)(ld)}, \tag{57a}$$

$$G_{(ia)(kc)} = g_{ik}g_{ac}. \tag{57b}$$

This makes inversion of the 4 index metric and the coefficient matrix substantially more straightforward (it may even be done explicitly under some conditions), and elsewhere we show that a noniterative local MP2 method can be formulated in this way.[26]

VI. CONCLUSIONS

We have employed a tensor formulation to extend many-electron theories from orthogonal representations of the occupied and virtual single-particle expansion spaces to the more general nonorthogonal case. Well-posed many-electron theories are invariant to details of the basis functions chosen for each subspace, as follows directly from the tensorial nature of the constituent quantities. Biorthogonality of many-electron bras and kets leads to tremendous simplifications compared to approaches which do not exploit this property, such as traditional nonorthogonal valence bond methods.

The equations of standard electron correlation methods such as MP2, CCSD, and CCSD(T) have not previously permitted nonorthogonality to this full extent. The additional generality of the equations given here offers, in our opinion, exciting possibilities for new local theories of electron correlation.[26]

ACKNOWLEDGMENTS

APPENDIX: TREATMENT OF EXACT LINEAR DEPENDENCE

Here we extend the tensor treatment to the case where exact linear dependence exists in the single-particle basis. The reason for doing so (rather than eliminating such redundancy at the outset) is that convenient sets of occupied and virtual functions may include exact linear dependence. A simple example are *projected atomic orbitals*, defined by acting with $\hat{P}$ and $\hat{Q}$ on the parent set of atomic orbitals:

$$|\phi_i\rangle = \hat{P}|\phi_\mu\rangle \delta_i^\mu = |\phi_\mu\rangle P_{\bullet\nu}^\mu \delta_i^\nu, \tag{A1}$$

$$|\phi_a\rangle = \hat{Q}|\phi_\mu\rangle \delta_a^\mu = (\hat{I} - \hat{P})|\phi_\mu\rangle \delta_a^\mu = |\phi_\mu\rangle (\delta_a^\mu - P_{\bullet\nu}^\mu \delta_a^\nu). \tag{A2}$$

The delta functions merely preserve index conventions. Projected atomic functions are localized to the same extent as the density matrix itself.[41] Their covariant metric matrices are the covariant representations of $\hat{P}$ and $\hat{Q}$, respectively,

$$g_{ij} = \langle \phi_i | \phi_j \rangle = \delta_i^\mu P_{\mu\nu} \delta_j^\nu, \tag{A3}$$

$$g_{ab} = \langle \phi_a | \phi_b \rangle = \delta_a^\mu (g_{\mu\nu} - P_{\mu\nu}) \delta_b^\nu. \tag{A4}$$

Contravariant functions may be defined by projection on the contravariant basis vectors with $\hat{P}$ and $\hat{Q}$; their contravariant metrics are the contravariant representations of $\hat{P}$ and $\hat{Q}$, respectively.

The *dimension* (number of linearly independent functions) of the occupied subspace is the particle number, n, but Eq. (A1) gives a larger set of functions (N). The metric matrix, Eq. (A3), is not then formally invertible, and the ability to change indices from covariant to contravariant seems to be lost. A coordinate transformation from a set of nonredundant functions to a linearly dependent representation (or vice versa) involves a rectangular matrix, which also has no formal inverse. Can we allow these redundant representations in the tensor formalism?

As has sometimes been recognized,[6] the answer is yes, for the following reason.[42] Trial vectors on which the inverse operates lie in the *range* of the metric (the linearly independent subspace) with no component in the *null space*, since a linearly dependent representation still spans the same space as a related linearly independent basis. Hence we employ a

generalized inverse based on discarding the null space, as defined by the singular value decomposition (SVD). Writing out summations explicitly, the SVD for a square matrix is

$$(S)_{ab}^{-1} = \sum_{c'} U_{ac} s_c^{-1} U_{bc}, \tag{A5}$$

where the terms in the sum over c are discarded if s_c (the eigenvalues of $\mathbf{S}$, with eigenvectors $\mathbf{U}$) is zero. This inverse does not satisfy $\mathbf{S}^{-1}\mathbf{S} = \mathbf{1}$, but does yield the correct solution, $\mathbf{x} = \mathbf{S}^{-1}\mathbf{b}$ to linear equations $\mathbf{Sx} = \mathbf{b}$, if $\mathbf{b}$ lies within the range of $\mathbf{S}$. The SVD is also general for rectangular matrices, as needed for transformations between redundant and nonredundant representations.

Generalized inverses of the metrics for projected atomic orbitals are the contravariant metric matrices discussed above: the density matrix and its orthogonal complement, respectively,

$$g^{ij} = \langle \phi^i | \phi^j \rangle = \delta_\mu^i P^{\mu\nu} \delta_\nu^j, \tag{A6}$$

$$g^{ab} = \langle \phi^a | \phi^b \rangle = \delta_\mu^a (g^{\mu\nu} - P^{\mu\nu}) \delta_\nu^b. \tag{A7}$$

This is proved either by considering the overlap of the contravariant projected functions themselves or by the fact that the product of these two matrices operating on any vector lying entirely within the occupied space yields the same function unmodified.

The contraction of the product of covariant and contravariant metrics yields an idempotent matrix which represents the Kronecker delta. For example, in the occupied case, we obtain

$$g^{ik} g_{kj} = \langle \phi^i | \phi_j \rangle = g_{\bullet j}^i \neq \delta_{\bullet j}^i. \tag{A8}$$

Thus redundant contravariant functions are not biorthogonal with redundant covariant functions. In the natural representation, $\hat{P}$ and $\hat{Q}$ must then be written as

$$\hat{P} = |\phi_i\rangle g_{\bullet j}^i \langle \phi^j|, \tag{A9}$$

$$\hat{Q} = |\phi_a\rangle g_{\bullet b}^a \langle \phi^b|. \tag{A10}$$

We next consider rectangular coordinate transformations, $C_{\bullet i}^{j'}$, from a set of projected atomic orbitals, Eq. (A1), (primed indices) to a linearly independent orthogonal set (unprimed indices). This transformation matrix is a set of molecular orbital coefficients. The generalized completeness relation above defines $\mathbf{C}$ and its generalized inverse $\mathbf{D}$ directly:

$$|\phi_i\rangle = |\phi_{j'}\rangle g_{\bullet k'}^{j'} \langle \phi^{k'} | \phi_i \rangle \equiv |\phi_{j'}\rangle C_{\bullet i}^{j'}, \tag{A11}$$

$$|\phi_{i'}\rangle = |\phi_j\rangle \langle \phi^j | \phi_{i'} \rangle \equiv |\phi_j\rangle D_{\bullet i'}^j = |\phi_j\rangle (C_{\bullet i}^{j'})^*. \tag{A12}$$

$\mathbf{D}$ is both a left inverse and a right inverse. In the latter case, where $\mathbf{D}$ is undoing the transformation into the unprimed coordinates, the product of $\mathbf{C}$ and $\mathbf{D}$ is not the identity matrix, but rather the projector onto the occupied subspace in the mixed representation. Thus $\mathbf{D}$ works properly on all functions in the occupied subspace. We can also view $\mathbf{D}$ as a transformation from an orthogonal basis into the linearly dependent representation, with $\mathbf{C}$ as its generalized inverse.

Let us now move from one-particle functions to many-particle functions. We must express all many-electron basis functions, such as the covariant reference ket and the substituted kets derived from it, in terms of redundant single-particle representations. The generalized permutation tensor[10,43] offers an elegant route. In orthogonal coordinates, $\epsilon^{ij\cdots k}$ is defined as $+1$ when $ij\cdots k$ is a symmetric permutation of the number of indices, -1 for an antisymmetric permutation, and zero otherwise. This is closely related to the antisymmetrizer, and lets us write $|\Phi\rangle$ as

$$|\Phi\rangle = (n!)^{-1/2}\epsilon^{ij\cdots k}|\phi_i(1)\rangle|\phi_j(2)\rangle\cdots|\phi_k(n)\rangle, \quad \text{(A13)}$$

where the number of indices is equal to the number of electrons.

In nonorthogonal representations, the values of $\epsilon^{ij\cdots k}$ are not integers, but instead represent the volume of a multidimensional parallelpiped with sides described by the functions $|\phi_i\rangle, |\phi_j\rangle, \ldots, |\phi_k\rangle$. $\epsilon^{ij\cdots k}$ is a relative tensor of rank 0 and weight $+1$ (with respect to transformations amongst the occupied levels). Therefore Eq. (A13) is valid in nonorthogonal basis sets also. Furthermore, Eq. (A13) is defined even if the number of levels (i.e., the range of each index) is greater than the number of electrons, and hence it can be viewed as a generalized definition of a determinant.

This connection permits us to write the covariant reference ket in redundant representations, while retaining the transformation properties derived in nonredundant representations. *Or, we can equivalently derive equations in a nonredundant representation, and transform the final results to redundant representations if needed.* The final form of the MP2, CCSD, and CCSD(T) equations remains essentially unaltered in redundant representations.

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