Transition probability calculations for atoms using nonorthogonal orbitals

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Individual orbital optimization of wave functions for the initial and final states produces the most accurate wave functions for given expansions, but complicates the calculation of transition-matrix elements since the two sets of orbitals will be nonorthogonal. The orbital sets can be transformed to become biorthonormal, in which case the evaluation of any matrix element can proceed as in the orthonormal case. The transformation of the wave-function expansion to the new basis imposes certain requirements on the wave function, depending on the type of transformation. An efficient and general method was found a few years ago for expansions in determinants, spin-coupled configurations, or configuration state functions for molecules belonging to the D_{2h} point group or its subgroups. The method requires only that the expansions are closed under deexcitation and thus applies to restricted active space wave functions. This type of expansion is efficient for correlation studies and includes many types of expansions as special cases. The above technique has been generalized to the atomic, symmetry adapted case requiring the treatment of degenerate shells nl^N, with arbitrary occupation numbers $0 \leq N \leq 4l + 2$. A computer implementation of the algorithm in the multiconfiguration Hartree-Fock atomic-structure package for atoms allows the calculation of transition moments for individually optimized states. An application is presented for the B I $1s^2 2s^2 2p\ ^2P^o \rightarrow 1s^2 2s 2p^2\ ^2D$ electric dipole transition probability, which is highly sensitive to core-polarization effects.

I. INTRODUCTION

The standard multiconfiguration self-consistent-field (MCSCF) procedure optimizes the orbitals used in a configuration interaction (CI) calculation with some specific selection of configuration state functions (CSF's). As a result, matrix elements between two separately optimized states must take into account the nonorthogonality between the two sets of orbitals. Transition matrix elements for two nonorthogonal states can be calculated fairly readily from basic principles without any transformations if there are only a few orbitals and a few configurations. For large calculations and many open shells, the formulas rapidly become complicated. Traditionally, in quantum chemistry, they are computed in terms of the transition matrix elements of individual determinantal functions and these in turn are evaluated as the first- and second-order cofactors of orbital overlap matrices [1]. Prosser and Hagström [2] proposed the use of the unsymmetrical Choleski factorization for the rapid evaluation of the necessary cofactors. This method has been applied by Ågren et al. [3] to configuration interaction expansions of a few hundred configuration state functions.

In atomic physics, pairwise methods have prevailed with unrestricted nonorthogonality allowed only for determinantal expansions. Westhaus and Sinanoğlu [4], using a transformation proposed by King et al. [5], showed that for E1 transitions it was not necessary to transform all orbitals, only the symmetries of the current pair contributing to the transition by the $\Delta l = 1$ selection rule. Nicolaides and Beck [6] improved the efficiency further by applying a priori selection rules for which the survival rate was about 1 out of 10. They also treated radial overlaps below a cutoff criterion as zero. A similar procedure was used by Beck [7] for a study of E2 transitions where the selection rules are different. When expansions are in terms of vector coupled configuration state functions (eigenfunctions of the total angular and total spin momenta) a number of assumptions have been introduced. The use of transition states allowing a simultaneous optimization of the initial and final states has been suggested [8]. In the general relativistic atomic structure package (GRASP) [9] a linear combination of energy expressions is used as the optimizing energy functional so that the orbitals of the initial and final states are constrained to be the same. Another commonly used approximation treats the radial distributions as though they *were* exactly orthonormal, even if obtained via separate self-consistent-field calculations for the different configurations involved (for instance, in ATOMSPEC, Cowan's chain of programs [10]). Since we are interested simultaneously in all the configurations included in the multiconfiguration calculation, the advantage of having the best possible single configuration is kept, without formally introducing any nonorthogonality complications. A more rigorous approach has been attempted in the computer codes CIV3 [11] and MCHF-ASP [12] by extend-

ing the Fano-Racah algebra, which underlies the angular momentum theory, to allow a limited use of nonorthogonal orbitals [13], avoiding radial orbital transformations. The restrictions adopted in the computer codes [14,15], however, may cause serious limitations.

Another approach is one where the wave functions are transformed to a new radial basis so that the evaluation of operators between states can proceed as though the bases were orthonormal. A few years ago, an efficient method was found [16], which solves this problem in the case of a restricted active space (RAS) [17] configuration selection scheme. The method is not only efficient but also easy to program. It was first implemented for a somewhat less general type of wave function, namely, the complete active space (CAS) wave function, a special case of the RAS scheme. The resulting CAS state interaction (CASSI) program [18] is used in quantum chemistry to compute transition density matrices and arbitrary matrix elements such as overlap and Hamiltonian matrix elements over a basis consisting of separately optimized CAS self-consistent-field (CASSCF) wave functions [19,20].

The idea is based on a second quantization scheme for a nonorthogonal basis, proposed by Moshinsky and Seligman [21]. As an illustration, consider the second-quantized form of an operator, sandwiched between two determinantal functions, in a scheme with one single orthonormal orbital basis. The ket function is produced by a string of creation operators acting on the vacuum. The bra functional consists of the vacuum bra followed by a similar string of annihilators. Between them is the operator. In elementary textbooks on second quantization [22,23], it is shown (in tedious detail) how repeated application of the anti-commutation rules $[a_p^\dagger, a_q]_+ = \delta_{pq}$ and other anticommutators ultimately produces a result in agreement with the usual Slater-Condon rules. These are simple because the Kronecker δ functions are mostly zero. The same approach works also with nonorthonormal orbitals, but the anticommutators become instead $[a_p^\dagger, a_q]_+ = S_{pq}$, the elements of the orbital overlap matrix. The formula now becomes the sum, with varying sign, of a very large number of products of overlap matrix elements, in fact, it can be evaluated as a determinant by the so-called Slater-Löwdin rules [1].

Of course, our present problem is not the use of a single, nonorthonormal basis but rather the use of two different orthonormal bases. This problem is readily shown to be equivalent: The second-quantized form of the operator is easily transformed so that its creators are those of the ket state, but the annihilators are the same as for the bra. Then every nonzero anticommutator will be identical in form to the case considered earlier, so it is evident that the transformation of operator integrals to a mixed orbital basis allows us to compute matrix elements over a mixed determinant basis by the Slater-Löwdin rules.

Moshinsky and Seligman then realized that the use of two different, nonorthogonal orbital sets for bra and ket determinants would result in the simple, usual Slater-Condon rules if the two orbital sets formed a biorthonormal system, since everything depends solely on the over-

lap matrix elements. Soon after its birth, Moshinsky and Seligman's picture was shown to be very helpful in nuclear physics. It has been used in the N-center model [24] and the same formalism was further developed by introducing the notion of holes in nonorthogonal bases [25].

Of course, this does not in itself solve our problem since our two orbital sets will certainly not be biorthonormal. A weak partial solution has been widely used: the corresponding orbital method [26], originally introduced by Amos and Hall [27] for single determinantal wave functions built on unrestricted molecular orbitals. This method has been applied to CASSCF wave functions, for which the CI expansion space is invariant under orbital rotations within the inactive or within the active orbitals. Such rotations are used to bring the orbitals into "corresponding orbitals." The two sets are individually orthonormal but, if different, cannot be biorthonormal. They are, however, biorthogonal. In effect, the transition matrix elements are computed as if in a common orthonormal basis, but with an extra normalization factor for each determinant [5]. The point in the restriction to true orbital rotations, keeping each orbital set orthonormal, was the belief that the CI expansions in the new basis must be recomputed by a conventional CI program after the new basis was obtained.

However, the necessity to use CASSCF wave functions is in itself a hindrance and the ability to freely mix only the active orbitals (or the inactive) is a severe restriction. The corresponding orbitals have been used for general CI or MCSCF expansions to perform nonorthogonal molecular configuration interaction [28] and transition moment calculations [29,30], but in the proposed research the method is applied separately to each pair of Slater determinants. If selection rules indicate that a contribution may occur, the overlap matrix of orbitals present in the pair of determinants under consideration is diagonalized with two unitary matrices.

A few years ago, it was observed that formally, the CASSCF wave function allows a much larger class of orbital transformations. The orbital transformation matrix must be nonzero only in the portion coupling inactive with active or virtual or coupling active with virtual orbitals. It must be nonsingular, but need not be an orthogonal matrix. It could still be used as suggested above because such a transformation matrix can be factorized into a sequence of single-orbital transformations and any single-orbital transformation can, in the CAS expansion space, be exactly performed as long as it does not excite from the inactive to the active or from the active to the virtual space. This immediately solved the problem for CASSCF wave functions and for molecules with symmetry D_{2h} or its subgroups. The CAS restriction was natural at the time; the symmetry restriction arose from the fact that a single-orbital transformation could break the spin symmetry of the wave function expansion. A program implementation in terms of symmetry adapted states could not represent the symmetry-broken intermediates in the wave function expansion. The formulas would be formally correct, but the program implementation would prevent calculation of the symmetry-broken intermediates: they could not be represented in the wave

function expansion space. This problem was solved for the nonrelativistic molecular problems by an *ad hoc* formula where the result of two subsequent single-orbital transformations, identical apart from spin, were expressed as two consecutive spin-preserving operations.

The minimal class of orbital transformations that must be allowed in order to bring arbitrary orbital set pairs into agreement with the requirements of biorthonormal systems contains those that are brought to triangular form after suitable permutation of orbitals. Finding the triangular transformation matrix for a given overlap matrix is then equivalent to a lower and upper (LU) triangular matrices decomposition, as shown in Ref. [16].

The requirement on the wave-function expansion space to allow this class of transformations is that it be *closed under deexcitation*. For some preferred orbital ordering, if one or more orbitals in a determinant are replaced by lower-numbered orbitals, the result must be in the expansion space. For determinants, it is either another determinant in the expansion space or zero. It was realized early that the RASSCF generalization [17,31] to the CASSCF has this property and the CASSI program was rewritten accordingly to become a RASSI.

Biorthonormal orbitals are now extensively used in the finite-element MCSCF LUCAS program [32], where the algorithm of countertransformations is applied to Slater determinant CI expansions. Since the Slater determinant basis does not make use of the full atomic symmetry, one can transform each spin-orbital separately. This has been used in multiconfiguration Hartree-Fock (MCHF) calculations with more than 10×10^6 Slater determinants [33].

In this paper we present a development on the use of restricted active space symmetry-adapted CI expansions in atomic transition probability calculations, involving the treatment of degenerate shells nl^N, with arbitrary occupation numbers $0 \le N \le 4l + 2$. The paper is organized as follows. After this introduction, there is a section on the restricted active space, another on nonorthogonal second quantization, and one on the details of transformation of orbitals and CI coefficients. This is followed by a section describing the program structure and finally one with an illustrative application, namely, the BI $1s^2 2s^2 2p \, ^2P^o \rightarrow 1s^2 2s 2p^2 \, ^2D$ oscillator strength, which is highly sensitive to core-polarization effects.

II. RESTRICTED ACTIVE SPACE CONCEPT

The CAS method [19] forms a cornerstone of the multiconfiguration approach: It has been used successfully for describing the static part of the electronic correlation energy of molecular systems [20]. The CASSCF wave function is a superposition of *all* the configurations in the N-electron space that fulfill two simple requirements: A certain number of *inactive* orbitals are always occupied and another specified number of *active* orbitals have varying occupancy. The inactive and active orbitals are optimized to make the energy stationary. Of course, the expansion space is further limited by any space- or spin-symmetry requirements and by specification of the total electron count, but this can hardly be considered a restriction. In the algebraic approximation, the results

are limited in precision by the finite basis set used, but it is usually not very difficult to saturate the basis set and obtain a basis set limit, so the obtained results are essentially a function of just the active space selection. The number of configurations is a polynomial with degree equal to the number of correlated electrons. Already with a few electrons, the CAS configuration space becomes quickly unmanageably large when the number of active orbitals is increased. Thus the CASSCF method is essentially an orbital method, similar to SCF, but able to manage near-degeneracy and open-shell problems. It is seldom able to include much dynamic correlation.

A RAS form of the wave function, introduced by Olsen *et al.* [17], encompasses many commonly used restricted configuration interaction expansions. In the RAS scheme, the restricted configuration space is determined from two different orbital spaces: the inactive space where all shells are filled and the active orbital space, which is further divided into three orbital subspaces: RAS-1, for which the total occupation of the orbitals must be at least some lower limit ($n_1 \ge N_1$); RAS-2, with no constraint imposed, and RAS-3, for which the total occupation of the orbitals may be at most an upper limit ($n_3 \le N_3$). In any configuration, the distribution of electrons from RAS-2 is then determined by the conservation of the total number of active electrons in the system $n_2 = N - n_i - n_1 - n_3$, where n_i is the number of inactive electrons in closed shells. Since the number of electrons from RAS-2 is unrestricted, the resulting configuration space is reminiscent of the original normal active space CAS.

There are basically two ways of using RAS expansions. The orbitals in RAS-1 will normally correspond to deep valence or core orbitals that should be correlated or polarized. The orbitals of RAS-2 correspond to valence orbitals including near-degeneracy orbitals. The orbitals in RAS-3 are additional orbitals introduced in order to polarize or correlate the orbitals in RAS-1 and RAS-2. Another interesting distribution is the following: RAS-1 would contain the orbitals of a zeroth-order wave function, RAS-2 the most important correlating orbitals, and the less important correlating orbitals would be put in RAS-3. By allowing fourfold excitations out of RAS-1 and only double excitations into RAS-3, one obtains CI expansions that contain the major part of triple and quadruple corrections in a compact fashion.

The RAS concept offers a number of advantages.

(i) It allows the use of very general types of CI expansions, providing systematic checks of the errors induced by truncating the CI expansion.

(ii) The RAS expansions satisfy the *closure under deexcitation* property, i.e., removing one electron from a subshell nl and placing it in any subshell $n'l$ of the same spatial symmetry with $n' < n$, we generate a configuration state function that appears in the original configuration interaction expansion. For subshells belonging to the same subspace, the restriction $n' < n$ is not necessary, giving closure for a limited set of excitations.

(iii) RAS expansions support a group of orbital transformations that allow the use of fully *biorthonormal* orbitals in the sense of Moshinsky and Seligman.

Properties (ii) and (iii) will be intensively used in the present transition probability calculations.

III. SECOND QUANTIZATION WITH NONORTHONORMAL ORBITALS

The material in this section is essentially that presented by Moshinsky and Seligman in a paper on the use of nonorthogonal orbital sets in a second-quantization formalism. Any reader familiar with tensor algebra in the Einstein notation will be delighted to discover that simple, systematic use of upper and lower index placement can be used to the same effect. The "direct" or "normal" orbitals are the carrier-space basis functions and should have a lower index. Lowering and raising is done by a metric, whose doubly covariant form is the orbital overlap matrix. This alternative presentation is convenient in some applications. (It is less useful in situations where many different equivalent bases appear.)

Consider a set of linearly independent spin orbitals with the general metric

$$\int d\mathbf{r}\, dm_s \varphi_p^*(\mathbf{r}, m_s)\varphi_q(\mathbf{r}, m_s) = \langle p|q\rangle \equiv S_{pq} , \tag{1}$$

where p, in the atomic case, may stand for the quantum numbers quartet $(n l m_s m_l)$. Introducing a new set of orbitals

$$(\tilde{\varphi}_1, \ldots, \tilde{\varphi}_m) = (\varphi_1, \ldots, \varphi_m)\mathbf{C} \tag{2}$$

and choosing $\mathbf{C}$ to be of the form

$$\mathbf{C} = \mathbf{S}^{-1/2}\mathbf{X} , \tag{3}$$

where $\mathbf{X}$ is a unitary matrix, the new orbitals constitute an orthonormal set

$$\tilde{S}_{ij} = (\mathbf{C}^\dagger \mathbf{S}\mathbf{C})_{ij} = \delta_{ij} . \tag{4}$$

(The special case $\mathbf{X} = \mathbf{I}$ is known as the "symmetric orthogonalization" [34].) The sets of creation operators corresponding to the original (nonorthogonal) $a^\dagger$ and transformed (orthonormal) $\tilde{a}^\dagger$ orbitals are related to each other in the same way as the orbitals themselves, since they must create the relevant orbitals if applied to the vacuum state. Let the $\mathbf{a}^\dagger$ stand for a row vector

$$\tilde{\mathbf{a}}^\dagger = \mathbf{a}^\dagger \mathbf{C} . \tag{5}$$

The creation and annihilation operators in the orthonormal basis $\tilde{\mathbf{a}}^\dagger$ satisfy the usual anticommutation relations [35,23]

$$\tilde{a}_i^\dagger \tilde{a}_j + \tilde{a}_j \tilde{a}_i^\dagger = \delta_{ij} ,$$
$$\tilde{a}_i^\dagger \tilde{a}_j^\dagger + \tilde{a}_j^\dagger \tilde{a}_i^\dagger = 0 , \tag{6}$$
$$\tilde{a}_i \tilde{a}_j + \tilde{a}_j \tilde{a}_i = 0 ,$$

from which we can deduce

$$a_m^\dagger a_n^\dagger + a_n^\dagger a_m^\dagger = \sum_{p,q} C_{pm}^{-1} C_{qn}^{-1}(\tilde{a}_p^\dagger \tilde{a}_q^\dagger + \tilde{a}_q^\dagger \tilde{a}_p^\dagger) = 0 , \tag{7}$$

$$a_m a_n + a_n a_m = (a_n^\dagger a_m^\dagger + a_m^\dagger a_n^\dagger)^\dagger = 0 . \tag{8}$$

These have the same form as for the orthonormal case.

However, the remaining anticommutation relation becomes

$$a_m^\dagger a_n + a_n a_m^\dagger = \sum_{p,q} C_{pm}^{-1} C_{qn}^{-1*}(\tilde{a}_p^\dagger \tilde{a}_q + \tilde{a}_q \tilde{a}_p^\dagger)$$

$$= \sum_{p,q} C_{pm}^{-1} C_{qn}^{-1*} \delta_{pq}$$

$$= (\mathbf{C}^{-1T}\mathbf{C}^{-1*})_{mn} = S_{nm} , \tag{9}$$

where we used the Hermiticity of $\mathbf{S}$ and Eq. (6) to show that $\mathbf{C}^{-1T}\mathbf{C}^{-1*} = \mathbf{S}^T$. Clearly the anticommutation relations satisfied by the creation and annihilation operators for a nonorthogonal basis differ from the normal ones by the appearance of the overlap matrix $\langle n|m\rangle$ instead of the Kronecker delta δ_{nm}.

The second-quantization form of the operators in a nonorthogonal basis $\{\varphi\}$ can be deduced straightforwardly from their form in the orthogonal basis $\{\tilde{\varphi}\}$ using the transformation Eq. (5). We have, for example, for the one-electron operator

$$\hat{h} = \sum_{p,q} \tilde{h}_{pq} \tilde{a}_p^\dagger \tilde{a}_q \tag{10}$$

$$= \sum_{p,q} (\mathbf{C}\mathbf{C}^\dagger \mathbf{h}\mathbf{C}\mathbf{C}^\dagger)_{pq} a_p^\dagger a_q$$

$$= \sum_{p,q} (\mathbf{S}^{-1}\mathbf{h}\mathbf{S}^{-1})_{pq} a_p^\dagger a_q , \tag{11}$$

where $\tilde{h}_{pq} = \langle \tilde{p}|h|\tilde{q}\rangle$ is the one-electron integral in the orthogonal basis.

While this formula is in perfect analogy to the orthonormal case, it is very unsuitable for most applications. The reason is that the operator a_q, which is the Hermitian conjugate of $a_q^\dagger$, does not act properly as an annihilator. A determinant can be written as a string of creators acting on the vacuum; preceding this with the operator a_q and then using Eq. (9), the result can be expressed in occupation-number representation as

$$a_q|\mathbf{n}\rangle = \sum_p \Gamma(\mathbf{n})_p S_{qp} n_p |n_1 \cdots 0_p \cdots n_m\rangle . \tag{12}$$

The occupation number array $\mathbf{n}$ with elements n_i specifies the occupation number (0 or 1) of the spin orbital i and

$$\Gamma(\mathbf{n})_i = (-1)^{\left[\sum_{j=1}^{i-1} n_j\right]} .$$

We see that a_q does not annihilate orbital q alone and the result is not a single determinant.

However, a linear combination of operators such as a_q can be used as an annihilator. Define $\hat{a}_q = \sum_r S_{qr}^{-1} a_r$. Using $\mathbf{a}$ to denote a column vector, we can also write

$$\hat{\mathbf{a}} = \mathbf{S}^{-1}\mathbf{a} . \tag{13}$$

The matrix multiplication with the inverse of $\mathbf{S}$ will counteract the $\mathbf{S}$ appearing in Eq. (9), giving the new anticommutation rule

$$a_i^\dagger \hat{a}_j + \hat{a}_j a_i^\dagger = \delta_{ij} , \tag{14}$$

The one-electron operator $\hat{h}$ can now be written as

$$\hat{h} = \sum_{p,q} (\mathbf{S}^{-1}\mathbf{h})_{pq} a_p^\dagger \hat{a}_q \ , \tag{15}$$

which may be defined as the second-quantization form of the operator. The $\hat{a}_q$ operator here acts as expected for an annihilator:

$$\hat{a}_q |\mathbf{n}\rangle = \Gamma(\mathbf{n})_q n_q |n_1 \cdots 0_q \cdots n_m\rangle \ . \tag{16}$$

This is the most suitable form for computations. Each term in the second-quantized form simply performs an orbital replacement, if possible, with precisely the same sign rules as if an orthogonal orbital set had been used. The price to pay is that a Hermitian *operator* is no longer represented by a Hermitian *matrix*.

The conjugate of the new operators define a set of new creators and thus orbitals. This relation between these new orbitals and the original ones is symmetric and one says that one basis is the dual of the other. The two bases are said to form a biorthonormal system since

$$\int d\mathbf{r}\, dm_s \hat{\varphi}_p^*(\mathbf{r}, m_s)\varphi_q(\mathbf{r}, m_s) = \langle \hat{p}|q\rangle = \langle 0|\hat{a}_p a_q^\dagger|0\rangle = \delta_{pq} \ . \tag{17}$$

If the two-orbital sets also span the same space, as we have assumed here, they are jointly called a biorthonormal basis. Two sets of determinantal functions, identical in definition except that two biorthonormal orbital sets are used, form a biorthonormal system of determinantal functions. The same is true for most types of spin and angular momentum coupled configuration state functions: If they are orthonormal when orthonormal orbitals are used, then they form biorthonormal systems when biorthonormal orbitals are used. However, they do not in general span the same space, unless a full CI expansion space is used.

The above analysis is essentially that of Moshinsky and Seligman [21]. Its essence is that by using the *ordinary* orbital basis for ket functions and creators and the *dual* basis for bra functionals and annihilators, then any formulas that can be proved by anticommutation relations will remain true also for the nonorthogonal case.

They showed, specifically, that the matrix elements of one- and two-body operators $F = \sum_i f_i$ and $G = \sum_{i<j} g_{ij}$ between a *dual* Slater determinant (SD)

$$\frac{1}{\sqrt{N!}}\mathcal{A}\hat{\varphi}_\alpha(1)\cdots\hat{\varphi}_\mu(n) \tag{18}$$

as the bra and an *ordinary* Slater determinant

$$\frac{1}{\sqrt{N!}}\mathcal{A}\varphi_\beta(1)\cdots\varphi_\nu(n) \tag{19}$$

as the ket have the same values as the matrix elements of the operators

$$\sum_{\xi,\eta} a_\xi^\dagger \langle \hat{\xi}|f|\eta\rangle \hat{a}_\eta \ , \tag{20}$$

$$\frac{1}{2}\sum_{\xi,\eta,\zeta,\lambda} a_\xi^\dagger a_\eta^\dagger \langle \hat{\xi}_1\hat{\eta}_2|g_{12}|\zeta_1\lambda_2\rangle \hat{a}_\zeta \hat{a}_\lambda \tag{21}$$

between the state

$$|\hat{\alpha},\ldots,\hat{\mu}\rangle \equiv \hat{a}_\alpha^\dagger \cdots \hat{a}_\mu^\dagger |0\rangle \tag{22}$$

as the bra and

$$|\beta,\ldots,\nu\rangle \equiv a_\beta^\dagger \cdots a_\nu^\dagger |0\rangle \tag{23}$$

as the ket. The second-quantized expression of the one- and two-body operators is then formally identical to the one we know using an orthonormal set of single-particle states. That is the *first* key of our approach.

We will use configuration interaction expansions of configuration state functions $\Phi(\alpha_i LS\pi)$ for describing two different atomic states

$$\Psi_1(\alpha LS\pi) = \sum_\mu C_\mu^X \Phi^X(\alpha_\mu LS\pi) \ ,$$

$$\Psi_2(\alpha' L'S'\pi') = \sum_\mu C_\mu^Y \Phi^Y(\alpha_\mu L'S'\pi') \ . \tag{24}$$

Each CSF is a linear combination of Slater determinants. It is a spin and angular momentum $\mathbf{S}^2$ and $\mathbf{L}^2$ eigenfunction. The one-electron orbital basis functions are products of angular momentum functions and radial functions, i.e., $\varphi_{nlm_l}(r,\theta,\phi) = (1/r)P_{nl}(r)Y_{lm_l}(\theta,\phi)$. The radial functions $\{P_{nl}^X\}$ are in general different from $\{P_{nl}^Y\}$ and we need to consider overlap integrals over the radial functions only. This simplifies calculations since the orbitals of each l quantum number can be considered separately and the overlap and transformation matrices are independent of m_l.

IV. TRANSFORMATION OF ORBITALS AND CI COEFFICIENTS

The contents of this section may be summarized as follows.

(i) The special choice of a LU (or, more precisely, a UL) decomposition of the inverse overlap matrices $\mathbf{S}^{-1}$ will define biorthonormal bases obtained by upper-triangular orbital transformation matrices for transformations defined by Eq. (2) where the orbital basis is considered as a row vector.

(ii) An upper-triangular orbital transformation matrix can be expressed as a finite sequence of single-orbital transformations. Each expresses the new orbitals as a sum involving no higher-numbered orbital.

(iii) The nontrivial effect of each such transformation step on the CI expansion array is the same as the effect of a one-electron operator with deexcitations only.

(iv) With a RAS wave function, such operations are *exactly* representable and the needed data structures are already available in a direct CI scheme.

(v) Some special procedures need to be introduced to simultaneously take advantage of the space and spin symmetry and yet avoid symmetry-breaking intermediates. Most of the details in the coming discussion appear also in the original article [16] on this method. However, different and important to the present application is the treatment of the last point: elimination of symmetry-breaking intermediates.

The transformation matrices $\mathbf{C}^{XA}$ and $\mathbf{C}^{YB}$ express the unknown biorthogonal sets $\{\varphi^A\}, \{\varphi^B\}$, in the original basis $\{\varphi^X\}, \{\varphi^Y\}$:

$$(\varphi_1^A, \ldots, \varphi_m^A) = (\varphi_1^X, \ldots, \varphi_m^X) \mathbf{C}^{XA} \ ,$$

$$(\varphi_1^B, \ldots, \varphi_m^B) = (\varphi_1^Y, \ldots, \varphi_m^Y) \mathbf{C}^{YB} \ . \tag{25}$$

To fulfill the biorthonormality condition

$$\langle \varphi_i^A | \varphi_j^B \rangle = \delta_{ij} \ , \tag{26}$$

the transformation matrices should satisfy the condition

$$\mathbf{C}^{YB} \mathbf{C}^{XA\dagger} = (\mathbf{S}^{XY})^{-1} \ . \tag{27}$$

In the above, the overlap matrix has been assumed to be square, but, as shown in Appendix B, this restriction may be removed.

There are infinitely many pairs of transformation matrices that will produce biorthonormal basis sets. The choice adopted in the present approach is predicted by the restrictions on the configuration state function spaces used for Ψ_1 and Ψ_2. We require the transformation matrices to be upper triangular. That this is a suitable choice will become evident from the effect of the transformation on the CI coefficients. For the moment, the $\mathbf{C}^{XA}$ matrix is assumed to be given.

The original set of orbitals or, equivalently, creators $\mathbf{a}^{X\dagger}$ are transformed into the nonorthogonal $\mathbf{a}^{A\dagger}$ set

$$a_k^{A\dagger} = \sum_l a_l^{X\dagger} C_{lk}^{XA} \ . \tag{28}$$

We want then to find the CI vector $\mathbf{C}^A$ that satisfies

$$\sum_\mu C_\mu^X | \Phi_\mu^X \rangle = \sum_\mu C_\mu^A | \Phi_\mu^A \rangle \ . \tag{29}$$

In Ref. [16] it is shown how this can be done by a finite sequence of single-orbital transformations.

The simplest way to proceed is to find out what happens when one single orbital k is reexpressed in the other orbitals. At this stage, several orbitals may already have been transformed. The present orbital set is denoted with primes, the next, with one orbital more transformed, is denoted with double primes:

$$a_k'^{\dagger} = \sum_{l \neq k} t_{lk} a_l'^{\dagger} + t_{kk} a_k''^{\dagger} \ . \tag{30}$$

Any determinantal function is a string of distinct creators acting on the vacuum. Reexpression of a determinant in the primed system using the double primed orbitals will, by the above formula, either leave it as it is (if the creator $a_k'^{\dagger}$ is not in this string) or else the creator $a_k'^{\dagger}$ is replaced by a sum of creators according to the above formula. This can be written generally as

$$| \Phi' \rangle = \left[1 + \sum_l (t_{lk} - \delta_{lk}) a_l''^{\dagger} \hat{a}_k'' \right] | \Phi'' \rangle \tag{31}$$

if Φ denotes any determinantal function of a selection of orbitals. Note that no complicated algebra is needed for the annihilator $\hat{a}_k''$: it merely expresses the removal of orbital k from the determinant, the caretted operators acting as proper annihilators, as explained in Eq. (16) and the reasoning behind that equation. Then this formula works also for any spin-coupled configurations, whether Serber functions, unitary group approach, or whatever, since those are simply fixed linear combinations of deter-

minantal functions. Thus, with any wave function basis, the CI expansion will fulfill

$$\sum_\mu C_\mu' | \Phi_\mu' \rangle = \sum_\mu C_\mu'' | \Phi_\mu'' \rangle$$

$$= \left[1 + \sum_l (t_{lk} - \delta_{lk}) a_l''^{\dagger} \hat{a}_k'' \right] \sum_\mu C_\mu' | \Phi_\mu'' \rangle \ . \tag{32}$$

Here, the first equality shows, by definition, that the two CI expansions should express the same wave function. The first and last members are equal because of the preceding formula (31). It follows that the two last members are equal, which provides the necessary connection between $\mathbf{C}'$ and $\mathbf{C}''$. Any CI program has the capability to express the result, on the CI expansion vector, of applying an exciting operator such as $a_l''^{\dagger} \hat{a}_k''$. For the particular case of a RAS wave function, the result will be exact if always $l \leq k$. The expansion vector $\mathbf{C}''$ can thus be obtained by performing a direct CI calculation with a one-electron operator having one index fixed (k).

The *general* transformation can then be obtained through the single orbital replacements sequence

$$\varphi_1^X = \varphi_1^A t_{11} + \varphi_2^X t_{21} + \varphi_3^X t_{31} + \cdots \ ,$$

$$\varphi_2^X = \varphi_1^A t_{12} + \varphi_2^A t_{22} + \varphi_3^X t_{32} + \cdots \ ,$$

$$\vdots$$

$$\varphi_k^X = \varphi_1^A t_{1k} + \varphi_2^A t_{2k} + \varphi_3^A t_{3k} + \cdots + \varphi_{k-1}^A t_{(k-1)k}$$

$$+ \varphi_k^A t_{kk} + \varphi_{k+1}^X t_{(k+1)k} + \cdots \ ,$$

$$\vdots \tag{33}$$

The replacement of step k consists in replacing $a_k^{X\dagger}$ by $a_k^{A\dagger}$

$$a_k^{X\dagger} = \sum_{l \leq k} a_l^{A\dagger} t_{lk} + \sum_{l > k} a_l^{X\dagger} t_{lk} \ . \tag{34}$$

It can be written as

$$a_k^{X\dagger} = \sum_l (\mathbf{C}^{XA} \mathbf{t}^U + \mathbf{t}^L)_{lk} a_l^{X\dagger} \tag{35}$$

by splitting the matrix $\mathbf{t}$ into upper (U) and strictly lower (L) triangular parts. The fact that Eq. (35) should hold for *all* k values implies

$$\mathbf{C}^{XA} = (\mathbf{I} - \mathbf{t}^L)(\mathbf{t}^U)^{-1} \ . \tag{36}$$

Since the inverse of an upper-triangular matrix is upper triangular, we have

$$\mathbf{C}^{XA} = \mathbf{LU} \tag{37}$$

with

$$\mathbf{L} = \mathbf{I} - \mathbf{t}^L \tag{38}$$

and

$$\mathbf{U} = (\mathbf{t}^U)^{-1} \ , \tag{39}$$

$\mathbf{L}$ being a lower-triangular matrix and $\mathbf{U}$ an upper-triangular matrix. Similar considerations apply for the transformation $\mathbf{C}^{YB}$ and CI countertransformations bringing Ψ_2 in its biorthonormal form.

Let us now return to the determination of $\mathbf{C}^{XA}$ and $\mathbf{C}^{YB}$. Substituting Eq. (36), but adding additional superscripts to distinguish the matrices transforming $\mathbf{C}^{XA}$ from $\mathbf{C}^{YB}$, into Eq. (27) we get

$$(\mathbf{I}-\mathbf{t}^{LYB})(\mathbf{t}^{UYB})^{-1}(\mathbf{t}^{UXA\dagger})^{-1}[\mathbf{I}-(\mathbf{t}^{LXA\dagger})]=(\mathbf{S}^{XY})^{-1} \ . \tag{40}$$

If we require the transformation matrices to be upper triangular, from Eq. (27), it is immediately seen that $\mathbf{S}^{-1}=\mathbf{U}^{XY}\mathbf{L}^{XY}$, or another exercise in decomposition. More precisely $\mathbf{C}^{YB}=\mathbf{U}^{XY}$ and $\mathbf{C}^{XA\dagger}=\mathbf{L}^{XY}$. In fact, this choice of triangular matrices will mean that in the partitioning described in Eq. (36),

$$\mathbf{t}^{LYB}=0, \quad \mathbf{t}^{LXA}=0 \ ,$$

$$\mathbf{t}^{UYB}=(\mathbf{U}^{XY})^{-1}, \quad \mathbf{t}^{UXA}=(L^{XY\dagger})^{-1} \ .$$

The reason that the detailed formulation above has been kept is that this works still if $\mathbf{C}^{XA}$ and $\mathbf{C}^{YB}$ are not just upper-triangular but *block*-upper-triangular matrices with orbitals collected into the four main orbital types: inactive, RAS-1, RAS-2, and RAS-3. As shown in Ref. [16], the transformation of inactive orbitals can be taken out as a single scale factor and the virtual orbitals can of course be simply ignored. The extra freedom allowed by general rather than triangular diagonal blocks can be used to gain extra numerical stability in certain cases.

Finally, we need to refine the method to avoid symmetry-breaking intermediates. To do this, we first order the spin orbitals so that those equivalent by symmetry are ordered contiguously. We now observe that the transformation of every component of such a subshell will have identically the same transformation coefficients, which depend only on radial overlaps, and that the components transform independently of each other, i.e., they may be transformed in any arbitrary order with the same result. For the subshell (nl) under consideration, Eq. (31) tells us that the transformation is equivalent to the application of an operator product

$$\prod_{k=1}^{g} \left[\hat{1}+\sum_{n'}(t_{n'n}-\delta_{n'n})a_{n'k}^{\dagger}\hat{a}_{nk}\right]\Psi \ , \tag{41}$$

where $k=1,2,\ldots,$ $(g\equiv 4l+2)$ enumerates the equivalent components (m_l,m_s), while n stands for the particular radial function $P_{nl}(r)$, and $n'\le n$, if we strictly follow the above scheme. Any other indices are irrelevant and have been omitted. To evaluate this without breaking symmetry, we first rewrite each factor as

$$\left[\hat{1}+\sum_{n'}(t_{n'n}-\delta_{n'n})a_{n'k}^{\dagger}\hat{a}_{nk}\right]$$

$$= \left[\hat{1}+\sum_{n'\ne n}s_{n'}a_{n'k}^{\dagger}\hat{a}_{nk}\right]t_{nn}^{\hat{N}_{nk}} \ , \tag{42}$$

where we define $s_{n'}\equiv t_{n'n}/t_{nn}$, and the last factor simply scales by t_{nn} those determinants of Ψ where spin orbital nk is occupied. Since this factor commutes with all the remaining factors in large parentheses in Eq. (41), it can be moved to the end. Repeating this with all the factors gives

$$\prod_{k=1}^{g} \left[\hat{1}+\sum_{n'}(t_{n'n}-\delta_{n'n})a_{n'k}^{\dagger}\hat{a}_{nk}\right]\Psi$$

$$= \prod_{k=1}^{g} \left[\hat{1}+\sum_{n'\ne n}s_{n'}a_{n'k}^{\dagger}\hat{a}_{nk}\right]t_{nn}^{\hat{N}_n}\Psi \ , \tag{43}$$

where the factor in front of Ψ scales each configuration with t_{nn} raised to the power given by the occupation number of shell n in the configuration. The product is evaluated via its logarithm

$$\ln\left[\hat{1}+\sum_{n'\ne n}s_{n'}a_{n'k}^{\dagger}\hat{a}_{nk}\right]=\sum_{n'\ne n}s_{n'}a_{n'k}^{\dagger}\hat{a}_{nk} \ , \tag{44}$$

where we use the fact that the action of $(a_{n'k}^{\dagger}\hat{a}_{nk})^{j}$ will give no contribution for $j>1$ and $n'\ne n$. The logarithm of each factor commutes. Moreover, if we define $\hat{s}$ as the sum

$$\hat{s}\equiv\sum_{n'\ne n}s_{n'}\sum_{k=1}^{g}a_{n'k}^{\dagger}\hat{a}_{nk} \ , \tag{45}$$

it is easy to see that it is nilpotent of degree $g+1$

$$\hat{s}^{g+1}=\hat{0} \ . \tag{46}$$

The nilpotency of the logarithm $\hat{s}$ can be used to terminate the series

$$\prod_{k=1}^{g} \left[\hat{1}+\sum_{n'}(t_{n'n}-\delta_{n'n})a_{n'k}^{\dagger}\hat{a}_{nk}\right]\Psi$$

$$= \exp(\hat{s})t_{nn}^{\hat{N}_n}\Psi = \left[\sum_{N=0}^{g}\frac{1}{N!}\hat{s}^{N}\right]t_{nn}^{\hat{N}_n}\Psi \ . \tag{47}$$

The whole point in converting to a logarithmic expression is that all intermediate results, obtained when operating with $\hat{s}$, are now contained in the expansion space: Since it is a double tensor of rank zero with respect to spin and orbit, as shown in Appendix A, $\hat{s}$ preserves both spin and orbital symmetries when acting on a CSF.

The complete result is thus obtained by repeatedly applying the operator $\hat{s}$, scaling, and adding. If the triangular decomposition of $\mathbf{S}^{-1}$ was used, then the sums above are over $n'<n$ rather than $n'\ne n$ and $\hat{s}$ is seen to be a strictly deexciting operator.

V. PROGRAM STRUCTURE

The computer implementation of the biorthonormal basis algorithm in the MCHF-ASP programs [12] is now limited to the evaluation of the transition moments between two CI expansions, i.e.,

$$\left\langle\Psi_1\left|\sum_i\hat{O}(i)\right|\Psi_2\right\rangle \ ,$$

where $\hat{O}(i)$ is an electric or magnetic multipole transition operator of any tensorial order [36]. The basic steps performed by the transition probability program can be summarized as followed.

(i) Check whether the CI expansions used for Ψ_1 and Ψ_2 satisfy the closure under deexcitation property.

(ii) Calculate the CSF coupling coefficients $A_{ij}^{\mu\nu}$ appear-

ing in the expression of the excitation operator action on the CSF's, i.e.,

$$a_i^\dagger a_j |\Phi_\nu\rangle = \sum_\mu A_{ij}^{\mu\nu} |\Phi_\mu\rangle ,$$

and needed to perform the transformation of the CI coefficients [see step (iv)]. They are identical to the coefficients of the one-electron integrals $I(n_j l, n_i l)$ in the $\langle \Phi_\mu | H | \Phi_\nu \rangle$ matrix element (see Appendix A). These quantities are invariant under orbital transformations and give the matrix representation of the excitation operators mapping the CSF expansion. This step is carried out for both Ψ_1 and Ψ_2.

(iii) Calculate the one-electron orbital overlap matrix and decompose it into block-triangular factors to find the new radial functions $\{P_{nl}^A(r)\}$ and $\{P_{nl}^B(r)\}$, which are biorthonormal.

(iv) Use the method outlined in Sec. IV to transform the configuration interaction eigenvectors $\mathbf{C}^A$ and $\mathbf{C}^B$ by a sequence of single-orbital replacements. That step is performed for each l symmetry, considering excitation operators

$$P_{n_j l}(r) \rightarrow P_{n_k l}(r) \text{ with } i \leq j ,$$

which satisfy the closure under deexcitation property of the CI expansions of Ψ_1 and Ψ_2.

(v) Use the *standard* (i.e., orthogonal) Racah-algebra "machinery" to transform the many-electron amplitude into a sum of one-electron reduced matrix elements [37]. The left- and right-hand side orbital indices of these refer now to the two *different* orbital *biorthonormal* sets.

The algorithm will apply to any CSF sets that are closed under deexcitation for both Ψ_1 and Ψ_2 expansions. The latter can include non-RAS-CI expansions that satisfy the closure under deexcitation property only within each irreducible representation, thereby still allowing the needed transformations.

The present approach does not constrain the inactive orbital spaces to be identical for the two states, unlike the corresponding orbitals method [26], which has been used for transition moment calculations [38]. The inactive shells are closed but core relaxation is allowed. Though Eq. (27) assumes identical numbers of shells on the left- and right-hand sides, the program can handle two wave functions that differ in dimensions in the RAS spaces. This more general case is considered in Appendix B.

There is presently a restriction in the CI program [39], which can deal with any number of s, p, or d electrons in a shell but with no more than two electrons in a shell with $l \geq 3$. If $l \geq 4$, the LS term for the shell is restricted to those allowed for $l = 4$. The presence of two f shells in the same subspace can violate the closure under deexcitation required property of the CI expansion. From a practical point of view, however, if f shells (or higher l angular momentum shells) are put in RAS-3 as correlating orbitals, there will be no problem, provided that we allow at most one or two electrons in that subspace.

The computer implementation of the algorithm has been tested by checking the invariance of the transition moment with respect to orbital rotations within the inac-

tive space or active subspaces (RAS) for which the transformed CSF vector(s) can be obtained for one (or both) states, by performing the CI calculation keeping the original CSF list(s). Since this invariance property is not related to the variational quality of the one-electron basis it has been checked to hold for any transition moment connecting any eigenvector of the left-hand side to any eigenvector of the right-hand side resulting from the CI diagonalizations. Another stringent test of the biorthonormal codes consisted in evaluating the transition probability between wave functions Ψ_1 and Ψ_2 build on a common orthonormal orbital set; in that case, the property can indeed be calculated exactly using existing codes [14,15] and an "artificially" rotated orbital set used for one of the two states involved can mimic a nonorthogonal situation.

VI. APPLICATION: THE $1s^2 2s^2 {}^2P^o \rightarrow 1s^2 2s 2P^2 {}^2D$ TRANSITION IN B I

The interaction between the configuration $1s^2 2s 2p^2$ and the Rydberg series $1s^2 2s^2 ns \, {}^2S$ and $1s^2 2s^2 nd \, {}^2D$ has been investigated recently by Carlsson *et al.* [40]. CAS multiconfiguration Hartree-Fock calculations of transition probabilities and lifetimes, with increasing active sets, have been performed keeping the $1s$ subshell *closed*. The agreement between calculated and experimental lifetimes is, in most cases, rather good. However, much less satisfactory results have been obtained for the $1s^2 2s^2 2p \, {}^2P^o \rightarrow 1s^2 2s 2p^2 \, {}^2D$ line. It has been argued that the disagreement between the length and velocity gf values is due to neglect of the strong core polarization by the $2s$ electron in $1s^2 2s 2p^2$. We investigated the core polarization of the $1s$ shell by performing multireference single- and double-excitation MCHF calculations. The two zeroth-order multireference wave functions are

$$\Psi^{(0)}({}^2P^o) = \{ 1s^2 2s^2 2p, 1s^2 2p^3 \, {}^2P^o \} ,$$

$$\Psi^{(0)}({}^2D) = \{ 1s^2 2s 2p^2, 1s^2 2s^2 3d \, {}^2D \} .$$

These calculations fit with the RAS concept, with the RAS-1 orbital subspace containing the $1s$ shell ($N_1 = 0$). The RAS-2 spaces contain $2s, 2p$ and $2s, 2p, 3d$ for ${}^2P^o$ and ${}^2D$, respectively. The correlation orbitals define the RAS-3 subset, with a maximum occupation number $N_3 = 2$.

The total energies and MCHF expansion lengths are reported in Table I for the increasing active sets, up to

TABLE I. SD multireference MCHF calculations in B I. $\Psi^{(0)}({}^2P^o) = \{ 1s^2 2s^2 2p, 1s^2 2p^3 \, {}^2P^o \}$ and $\Psi^{(0)}({}^2D) = \{ 1s^2 2s 2p^2, 1s^2 2s^2 3d \, {}^2D \}$.

n	$E \, {}^2P^o$ (a.u.)	No. of CSF's	$E \, {}^2D$ (a.u.)	No. of CSF's
HF	−24.529 061	1	−24.311 869	1
2	−24.560 354	6	−24.311 921	4
3	−24.621 891	129	−24.379 506	157
4	−24.638 480	520	−24.416 497	812
5	−24.645 478	1301	−24.424 768	2320
6	−24.648 728	2584	−24.429 451	5004
7	−24.650 290	4479	−24.431 353	9161

TABLE II. SD multireference MCHF gf values in B I. $1s^2 2s^2 2p\ ^2P^o \rightarrow 1s^2 2s 2p^2\ ^2D$.

N	gf_l	gf_v	S_l	ΔE (cm^{-1})
3	0.6876	0.8156	2.5534	53 197
4	0.2456	0.2696	0.9959	48 720
5	0.2625	0.2695	1.0705	48 440
6	0.2891	0.2866	1.1868	48 125
7	0.2928	0.2900	1.2036	48 051
Expt[a]	0.28(02)			47 857

[a]From Ref. [41].

$n = 7$. The corresponding length and velocity oscillator strengths, calculated with the theoretical transition energy differences, are given in Table II. The two formalisms converge very nicely to each other and to the experimental value. The final theoretical values reported in Table III are calculated using the experimental transition energies. They agree very well with the laser-induced fluorescence measurement of O'Brian and Lawler [41], demonstrating the $1s$ polarization effect.

APPENDIX A

Starting from the second-quantization form of the single-particle Hamiltonian operator

$$H = \sum_{\xi, \eta} a_\xi^\dagger \langle \xi | h | \eta \rangle a_\eta \ ,\tag{A1}$$

with the one-electron integral definition

$$I_{n'l,nl} \equiv -\frac{1}{2} \int_0^\infty P_{nl}(r) \left[\frac{d^2}{dr^2} + \frac{2Z}{r} - \frac{l(l+1)}{r^2} \right]$$
$$\times P_{n'l}(r) dr \ ,\tag{A2}$$

we simply have

$$H = \sum_l \sum_{n',n} I_{n'l,nl} \sum_{m_l, m_s} a_{n'lm_l m_s}^\dagger a_{nlm_l m_s} \ .\tag{A3}$$

To make more explicit the fact that this operator is scalar in both spin and orbital spaces, it is interesting to build the coupled tensor of ranks (00) [35]

$$(\mathbf{a}_{n'l}^\dagger \mathbf{a}_{nl})_{00}^{(00)} = -\frac{1}{\sqrt{2(2l+1)}} \sum_{m_l, m_s} a_{n'lm_l m_s}^\dagger a_{nlm_l m_s}\tag{A4}$$

TABLE III. Oscillator strengths for $1s^2 2s 2p\ ^2P^o \rightarrow 1s^2 2s 2p^2\ ^2D$ in B I.

Method	Length	Velocity
Theory		
CAS MCHF (1s closed)[a]	0.243	0.274
Weiss[b]	0.402	0.504
Sibincic[c]	0.690	0.942
Sinanoğlu and Davis[d]	0.216	
Nicolaides and Beck[e]	0.174	0.210
Nesbet[f]	0.292	
this work	0.292	0.291
Experiment		
phase shift[g]	0.28(09)	
beam foil	0.24(01)[h], 0.30(05)[i], 0.36(02)[j]	
	0.30(02)[k], 0.27(02)[l]	
level crossing[m]	0.28(03)	
laser induced fluores[n]	0.28(02)	

[a]From Ref. [40].   [h]From Ref. [49].
[b]From Ref. [43].   [i]From Ref. [50].
[c]From Ref. [44].   [j]From Ref. [51].
[d]From Ref. [45].   [k]From Ref. [52].
[e]From Ref. [46].   [l]From Ref. [53].
[f]From Ref. [47].   [m]From Ref. [54].
[g]From Ref. [48].   [n]From Ref. [41].

and use it to express Eq. (A3) simply as

$$H = -\sum_l \sqrt{2(2l+1)} \sum_{n',n} (\mathbf{a}_{n'l}^\dagger \mathbf{a}_{nl})_{00}^{(00)} I_{n'l,nl} \ .\tag{A5}$$

From Eq. (A3) it can be seen that the action of the needed excitation operators on the CSF's appearing in the transformation operator Eq. (47) can be naturally extracted from the one-electron integral list generated by the angular code [42].

APPENDIX B

In the biorthonormality of Eq. (26) nothing requires the number of orbitals on the left- and right-hand side to be identical for a given l value. Let n and m be the dimensions of the orbital bases ($\{\varphi^A\}$, $\{\varphi^X\}$) and ($\{\varphi^B\}$, $\{\varphi^Y\}$), respectively, with $m > n$. In that case, the $(n \times m)$ overlap matrix $\mathbf{S}^{XY}$ has the structure

$$\mathbf{S}^{XY} = (\mathbf{TZ}) \ ,\tag{B1}$$

where $\mathbf{T}$ is a square submatrix of order n and $\mathbf{Z}$ is a rectangular submatrix of dimensions $n \times (m-n)$. We want to find the transformation matrices $\mathbf{C}^{YB}$ and $\mathbf{C}^{XA\dagger}$ satisfying

$$\mathbf{C}^{XA\dagger} \mathbf{S}^{XY} \mathbf{C}^{YB} = (\mathbf{I0}) \ ,\tag{B2}$$

where $\mathbf{I}$ is the unit matrix of order n and $\mathbf{0}$ is the zero rectangular matrix of dimensions $(m-n) \times n$. Let us make the ansatz

$$\mathbf{C}^{YB} = \begin{bmatrix} \mathbf{C}_{11}^{YB} & \mathbf{C}_{12}^{YB} \\ \mathbf{0} & \mathbf{I} \end{bmatrix} \ ,\tag{B3}$$

where C_{11}^{YB} is a square matrix of order n. The condition (B2) corresponds to

$$C^{XA\dagger}TC_{11}^{YB}=I \qquad (B4)$$

and

$$C^{XA\dagger}TC_{12}^{YB}+C^{XA\dagger}Z=0 . \qquad (B5)$$

Equation (B4) can be used to obtain a pair of matrices $(C^{XA\dagger}, C_{11}^{YB})$. Once these are obtained, one can get C_{12}^{YB} as

$$C_{12}^{YB}=-(C^{XA\dagger}T)^{-1}C^{XA\dagger}Z . \qquad (B6)$$

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