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Application of unitary-group methods to composite systems

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The unitary-group approach is extended to the treatment of composite systems such as ionic states in molecules (ligands, etc.). Those are represented hierarchically in terms of SU(n)-based Weyl-Young tableaux which reflect the permutational symmetry of the ionic sites themselves labeled by SU(2) based tableaux which, in turn, reflect the internal electronic structure. Matrix elements of quantum-mechanical tensor operators, including both spin-independent and spin-dependent multipole-multipole interactions, are presented using corresponding spin-graphical representations. The hierarchy of the state definitions is shown to reveal the "fine structure" of the ionic interactions.

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I. INTRODUCTION

The purpose of this paper is to extend methods of the unitary-group approach (UGA) to treat cooperative phenomena involving ionic states in molecules, ligands, and lattices. Properties of such systems arise mainly due to electronic structure. It is particularly important, therefore, to account for the effects of electron correlation. Since the interactions involve electrons situated around differing ionic sites correlations must reflect both the permutational symmetry of electrons at each ionic site dictated by Pauli's principle and also that of the ions themselves as part of a larger system. The UGA is well suited to provide both a means for representing states and an efficient calculus for the evaluation of matrix elements of quantum-mechanical operators.

In Sec. II we show how states of an ionic system can be represented hierarchically in terms of (a) SU(n)-based tableux which reflect the permutational symmetry of the ionic sites and (b) by SU(2)-based tableau labels which reflect the internal electronic structure of each ion.

In Sec. III we discuss the evaluation of matrix elements of quantum-mechanical tensor operators, including both spin-independent and spin-dependent multipole-multipole interactions. Results are derived using techniques of spin-graphical analysis.

II. BASIC THEORY

We consider a system of N ionic sites in a molecular or ligand. As shown schematically in Fig. 1 the μth site is characterized by a rigidly fixed nucleus (alternatively, an ionic core consisting of nucleus screened by the electrons in closed orbitals), with effective charge Z_μ and mass m_μ in atomic units, and N_μ (valence) electrons attached to that site. This is the standard Born-Oppenheimer approximation where we assume separability of the total system wave function into electronic and nuclear (ionic core) parts, namely, $\Psi=\Psi_e\Psi_n$. Each subsystem is described by a Schrödinger equation,

$$H_e\Psi_e=E_e\Psi_e \ , \tag{2.1a}$$

$$(H_n+E_e)\Psi_n=E_n\Psi_n \ . \tag{2.1b}$$

The Hamiltonians are expressed as

$$H_n=-\tfrac{1}{2}\sum_{\mu=1}^{N}\nabla_\mu^2 \ , \tag{2.2}$$

$$H_e=-\tfrac{1}{2}\sum_{\mu=1}^{N}\sum_{i=1}^{N_{\mu i}}\nabla_{\mu i}^2+V_{ee}+V_{ne}+V_{nn} \ . \tag{2.3}$$

These operators contain the usual kinematic and Coulombic interaction terms, but are independent of spin. The term V_{nn} in (2.3) is assumed constant when applied in (2.1a) and all three V terms are parameterized both by electron coordinates relative to their ionic center and by the interionic distances.

We shall also assume an operator H_{spin} to be defined which refers collectively to spin-dependent terms including, for example, spin-orbit and spin-spin interactions.

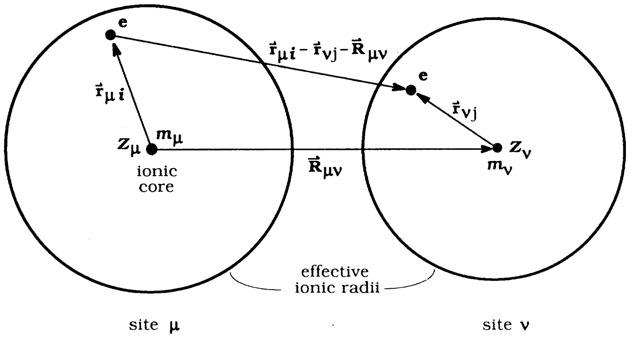

FIG. 1. Schematization of electron-ion structure showing vector relationships between interacting electrons from differing ionic sites.

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These may (or may not) be treated perturbatively.

Many-particle eigenstates can be constructed by adapting to permutation (spin) symmetry. This is accomplished using the techniques of the unitary-group approach whereby Young operators defined on the partitions of the group S_N are applied to products of single-particle wave functions to produce properly symmetrized linear combinations of orbital products. We assume that single-particle wave functions can be obtained and are labeled by ionic site, using Greek indices, and by the appropriate spatial-symmetry classifiers. For example, with atomic orbitals one might use the shell index, l and m_l labels, whereas in a molecule or ligand point-group symmetry indices would be preferred.

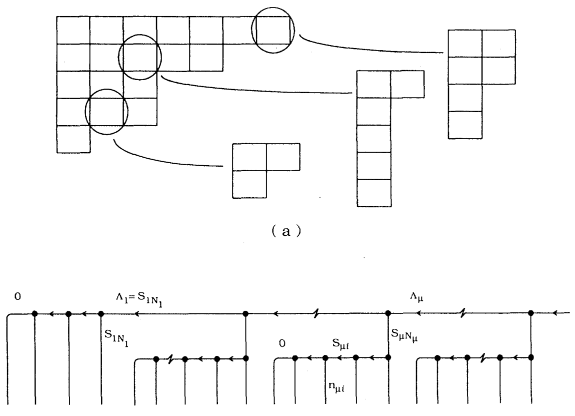
We assume the number of orbitals available to the electrons at site μ is n_μ and the total number of orbitals is $n=\sum_{\mu=1}^{N} n_\mu$. Furthermore, we assume that the N_μ electrons can be viewed as a quasiparticle. The model allows for transitions from one to another electronic orbital; hence, transitions between quasiparticle states are permitted. Taking into account the spin of each electron (labels $s=\frac{1}{2}$ and m_s) the electronic wave functions are constructed following the group chain,

$$U((2n)^N)\supset \sum_{[\Lambda]\ni N} \oplus(\mathrm{U}_{[\Lambda]}(n)\otimes \mathrm{SU}_{[\Lambda^*]}(n'))$$
$$\supset \sum_{[\Lambda]\ni N} \bigotimes_{\substack{\mu=1;\\ (\lambda)\ni[\Lambda]}}^{N} \left[\sum_{[\lambda_\mu]\ni N_\mu} \oplus(\mathrm{U}_{[\lambda_\mu]}(n_\mu) \otimes \mathrm{SU}_{[\tilde{\lambda}_\mu]}(2))\right], \tag{2.4}$$

where n' is the number of spin levels, $[\lambda_\mu]$ and $[\Lambda]$ denote irreducible representations (irreps) of S_{N_μ} and S_N, respectively, while $[\tilde{\lambda}]$ denotes the conjugate partition (tableaux) obtained by juxtaposing columns and rows. The notation $[\Lambda^*]$ implies the conjugate partition if the quasiparticles are fermionic (n' half-integral) and the same partition if the quasi-particles are bosonic (n' integral).

From the group chain (2.4) we note that states are represented hierarchically. In terms of the Weyl-Young tableux, states are expressed as products of multirow, multicolumn labeled Young frames where the μth box corresponds to the subensemble of electrons which constitute quasiparticle μ. The details of permutational symmetry for the electron ensemble comprising each quasiparticle is revealed in terms of a product of conjugate orbital and spin tableux. The statistical properties of quasiparticles are deduced from the total irrep spin associated with the electronic tableau structure (integral spin for bosons and half-integral for fermions). The nature of the tableau hierarchy is shown schematically in Fig. 2(a).

Equivalently, states can be built up using techniques from generalized angular-momentum-coupling theory. One convenient and useful representation of this approach uses generalized Yutsis diagrams, or spin graphs, as shown in Fig. 2(b). Each line of the graph is labeled by a complete set of partition indices (Λ_μ) or, where no ambiguity arises, by the total intermediate spin ($S_{\mu i}$). For each quasiparticle electrons are vector coupled to a resultant total spin, that is, products of orbital and spin tableaux which form irreps of $U(n_\mu)$. Then, the spins (partition indices) of the quasiparticles are coupled to form intermediate states which are irreps of the intermediate number of orbitals.



(a)

(b)

FIG. 2. Hierarchical structure of states: (a) the Weyl-Young tableau representation, and (b) spin-graphical representation.

Finally, it is to be emphasized that there need not be any special restrictions on the allowed sets of orbital labels for each quasiparticle system of electrons. These can include both pure and mixed configurations of orbitals. Tableau states can be further adapted to states labeled by, say, total L or other spatial symmetry, and S. This is accomplished by using ladder and projection operators [1–3].

With respect to the wave functions Ψ_n from (2.1b) these are represented as symmetry adapted ensembles of either nuclei or ionic cores with closed shells and filled orbitals. In either case the nuclei determine the space and spin properties used in labeling. Much of the early work on the unitary-group approach by Biedenharn and Louck [4] and co-workers was specifically directed at the dynamics of nuclear ensembles (using perturbed harmonic-oscillator models). We shall not discuss this issue further, therefore.

To summarize the results of this section, we have constructed states based on a hierarchical approach to coupling in which electron ensembles around ionic sites are

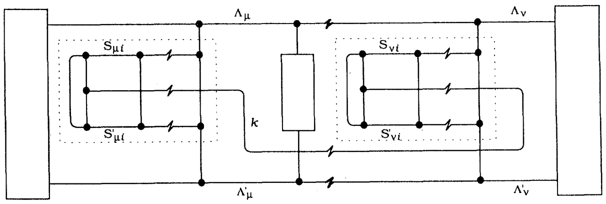


FIG. 3. Spin-graphical representation of one-body operator acting between electrons in neighboring ions.

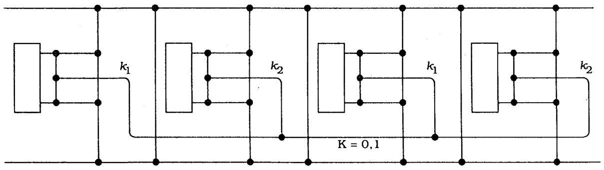


FIG. 4. Spin-graphical representation of two-body (multipole-multipole) operator matrix element illustrating singlet ($K=0$) and triplet ($K=1$) decomposition of exchange terms.

treated as quasiparticles with well-defined quantum-mechanical properties and these quasiparticles are coupled to form the electronic states of the many-ion system.

III. TENSOR OPERATOR MATRIX ELEMENTS

In this section we treat the evaluation of matrix elements of various operators within the context of the hierarchical basis functions discussed in the previous section. Of particular interest is the relationship between matrix elements of operators acting on the electronic quasiparticles versus those same states specified more directly in terms of the detailed electronic structure. In each subsection below we consider a different aspect of matrix element evaluation.

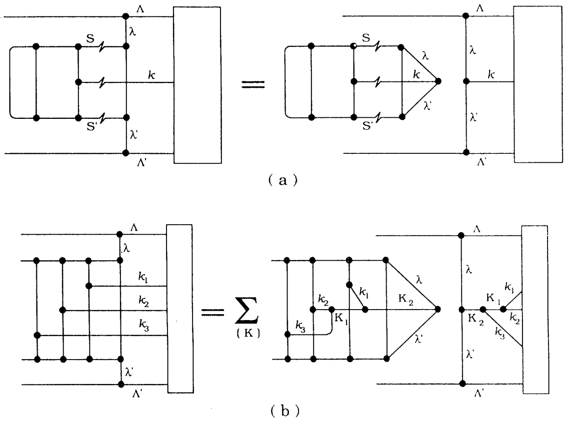


FIG. 5. Spin-graphical representation of (a) single-particle and (b) multiparticle operators acting on electron states within a quasiparticle.

A. Multipole operator matrix elements

We consider first the matrix elements of spin-independent tensor operators $T_q^{(k)}(\mu,\nu)$. Applying the Wigner-Eckart theorem within the quasiparticle representation the reduced matrix elements are typified by the graph in Fig. 3. Thus, we find the algebraic form,

$$\langle(\Lambda')\|T^{(k)}(\mu,\nu)\|(\Lambda)\rangle=\prod_{\alpha=1}^{\mu-1}\delta(\lambda_\alpha,\lambda'_\alpha)\prod_{\alpha=\nu}^{N}\delta(\lambda_\alpha,\lambda'_\alpha)d(k,\Lambda_{\mu-1},\Lambda'_\nu)\begin{Bmatrix}\Lambda_\mu & \lambda_\mu & \Lambda_{\mu-1}\\ \lambda'_\mu & \Lambda'_\mu & k\end{Bmatrix}$$

$$\times\prod_{\rho=\mu}^{\nu-1}\begin{Bmatrix}\Lambda_\rho & \Lambda'_\rho & \lambda_\rho\\ \Lambda'_{\rho-1} & \Lambda_{\rho-1} & k\end{Bmatrix}\begin{Bmatrix}\Lambda'_{\nu-1} & \lambda'_\nu & \Lambda_\nu\\ \lambda_\nu & \Lambda_\nu & k\end{Bmatrix}, \tag{3.1}$$

where $d(a,b,\ldots,)$ are the number of orbitals in irreps a, b and so on and quantities in braces are the SU(n) generalizations of the SU(2) Racah coefficients [5].

Taking into account the structure of the quasiparticles an amendment must be applied to expression (3.1). The exact form is dependent on the structure of the tensor operator, however. For $k=1$ and $T^{(k)}(\mu i,\nu j)$ a one-electron operator (e.g., transition, excitation) acting to transform the ith electron of system μ to the jth electron of system ν the amendment is

$$\langle[\Lambda';(\lambda')]\|T^{(k)}(\mu,\nu)\|[\Lambda;(\lambda)]\rangle=\langle(\Lambda')\|T^{(k)}(\mu,\nu)\|(\Lambda)\rangle\sum_{i=1}^{N_\mu}\sum_{j=1}^{N_\nu}C_{\Lambda,\Lambda'}(T^{(k)}(\mu i,\nu j)), \tag{3.1'}$$

where

$$C_{\Lambda\Lambda'}(T^{(k)}(\mu i,\nu j))=\prod_{k=1}^{i-1}\delta(S_{\mu k},S'_{\mu k})\prod_{k=1}^{j-1}\delta(S_{\nu k},S'_{\nu k})d(n_{\mu i},n_{\nu j})F_{\lambda_\mu,\lambda'_\mu}(i)F_{\lambda_\nu,\lambda'_\nu}(j), \tag{3.2}$$

and where

$$F^{(k)}_{\lambda_\mu,\lambda'_\mu}(i)=\begin{Bmatrix}\lambda_{\mu i} & \dfrac{n_{\mu i}}{2} & \lambda_{\mu i-1}\\ \dfrac{n'_{\mu i}}{2} & \lambda'_{\mu i} & k\end{Bmatrix}\prod_{k=i+1}^{N_\mu}\begin{Bmatrix}\lambda_{\mu k} & \lambda_{\mu k-1} & \dfrac{n_{\mu k}}{2}\\ \lambda'_{\mu k-1} & \lambda'_{\mu k} & k\end{Bmatrix}. \tag{3.3}$$

The parameter $n_{\mu i}$ is the occupation number for orbital i and is expressed as mod2 in (3.3) to account for singly and doubly occupied orbitals.

Multielectron operators, as shown in Fig. 4, are represented by tensor products such as

$$T^{(k)}_{k_1,k_2,q}=\sum_{\substack{q_1,q_2\\ q_1+q_2=q}} \sqrt{2k+1}(-1)^q \begin{bmatrix} k_1 & k & k_2 \\ q_1 & q & q_2 \end{bmatrix} T^{(k_1)}_{q_1}T^{(k_2)}_{q_2} \ . \tag{3.4}$$

Two-electron operators (3.4), for example, the Coulomb repulsion between two electrons from the same quasiparticle, have been studied by Drake and Schlesinger [6].

As an example of the type of operator, which does arise, we consider the multipole expansion of two neighboring quasiparticles,

$$\begin{aligned} V_{ee}(\mu,\nu) &= \sum_{i=1}^{N_\mu}\sum_{j=1}^{N_\nu} \frac{1}{\|\mathbf{r}_{\mu i}-\mathbf{r}_{\nu j}-\mathbf{R}_{\mu\nu}\|} \\ &= \sum_L \frac{1}{R_{\mu\nu}^{L+1}} \mathbf{C}^{(L)}(\hat{\mathbf{R}}_{\mu\nu})\cdot\mathbf{B}^{(L)}(\mu,\nu) \ , \end{aligned} \tag{3.5}$$

where $\mathbf{C}^{(L)}$ are the usual spherical tensors and

$$B^{(L)}_M(\mu,\nu)=\sum_{i=1}^{N_\mu}\sum_{j=1}^{N_\nu}\sum_{\substack{l_i,l_j\\ l_i+l_j=L}} (-1)^{l_j}\left[\frac{(2L)!}{(2l_i)!(2l_j)!}\right]^{1/2} r_{\mu i}^{l_i} r_{\nu j}^{l_j} \langle l_i l_j m_i m_j | LM\rangle C^{(l_i)}_{m_i}(\hat{\mathbf{r}}_{\mu i}) C^{(l_j)}_{m_j}(\hat{\mathbf{r}}_{\nu j}) \ . \tag{3.6}$$

Equations (3.5) and (3.6) constitute the multipole expansion of the Coulomb interaction between two systems of charges separated by $R_{\mu\nu}$ with the assumptions $R_{\mu\nu} > r_{\mu i}, r_{\nu j}$. Carets on the various radial vectors refer to the corresponding unit vectors along those directions. Each spherical tensor in (3.6) should be viewed as a single-electron transition operator or as a multielectron operator. Examples of such graphs are shown in Fig. 5.

B. Spin-dependent operator matrix elements

The spin-dependent part of the Hamiltonian H_{spin} usually consists of spin-orbit and spin-spin interaction terms. These interactions differ from the spin-independent ones primarily in the way in which states of different partitions of S_N are coupled by the respective tensor operators. To denote the fact that the operators act on the partitions we write them as $S^{(\Gamma)}_\gamma$ and $S^{(\Gamma)}_{\gamma_1,\gamma_2,\gamma}$. The type of graph representing a reduced matrix element which arises is shown in Fig. 6. This graph is expressed algebraically as

$$\begin{aligned} \langle(\Lambda')\|S^{(\Gamma)}_{\gamma_1,\gamma_2}(\mu,\nu)\|(\Lambda)\rangle &= \prod_{\rho=1}^{\mu-1}\delta(\Lambda_\rho,\Lambda'_\rho)\prod_{\rho=\nu}^{N}\delta(\Lambda_\rho,\Lambda'_\rho) d(\lambda_\mu,\lambda'_\nu) \begin{Bmatrix} \Lambda_\mu & \lambda_\mu & \Lambda_{\mu-1} \\ \lambda'_\mu & \Lambda'_\mu & k_1 \end{Bmatrix} \\ &\quad \times \prod_{\rho=\mu+1}^{\nu-1} \begin{Bmatrix} \Lambda_\rho & \Lambda_{\rho-1} & \lambda_\rho \\ \Lambda'_{\rho-1} & \Lambda'_\rho & \gamma_1 \end{Bmatrix} \begin{Bmatrix} \Lambda'_{\nu-1} & \Lambda_{\nu-1} & \gamma_1 \\ \Lambda'_\nu & \Lambda_\nu & \Gamma \\ \lambda'_\nu & \lambda_\nu & \gamma_2 \end{Bmatrix} \\ &\quad \times \prod_{\rho=\nu+1}^{N} \begin{Bmatrix} \Lambda_\rho & \Lambda_{\rho-1} & \lambda_\rho \\ \Lambda'_{\rho-1} & \Lambda'_\rho & \Gamma \end{Bmatrix} \ . \end{aligned} \tag{3.7}$$

Accounting for the internal electronic structure produces a multiplicative amending factor to (3.7), similar to (3.1)–(3.3), namely,

$$\langle(\Lambda';(\lambda'))\|S^{(\Gamma)}_{ee;\gamma_1,\gamma_2}(\mu,\nu)\|(\Lambda;(\lambda)\rangle = C^{(2)}_{\Lambda,\Lambda'}(S^{(\Gamma)}_{\gamma_1,\gamma_2}(\mu,\nu))\langle(\Lambda')\|S^{(\Gamma)}_{\gamma_1,\gamma_2}(\mu,\nu)\|(\Lambda)\rangle \ , \tag{3.7$'$}$$

where

$$C^{(2)}_{\Lambda,\Lambda'}(S^{(\Gamma)}_{\gamma_1,\gamma_2}(\mu,\nu)) = \langle(\lambda'_\mu)\|S^{(\gamma_1)}\|(\lambda_\mu)\rangle\langle(\lambda'_\nu)\|S^{(\gamma_2)}\|(\lambda_\nu)\rangle \ , \tag{3.8}$$

where, for $S^{(\gamma)}$ a one-electron spin operator, one finds the reduced matrix element

$$\langle(\lambda'_\mu)\|S^{(y)}\|(\lambda_\mu)\rangle = \sum_{i=1}^{N_\mu}\sum_{k=1}^{i=1}\delta(n_{\mu k},n'_{\mu k}) \begin{Bmatrix} S_{\mu i} & \dfrac{n_{\mu i}}{2} & S_{\mu i-1} \\ \dfrac{n'_{\mu i}}{2} & S'_{\mu i} & \gamma \end{Bmatrix} \prod_{j=i+1}^{N_\mu} \begin{Bmatrix} S_{\mu j} & S_{\mu j-1} & \dfrac{n_{\mu j}}{2} \\ S'_{\mu j-1} & S'_{\mu j} & \gamma \end{Bmatrix} \ . \tag{3.9}$$

We note that matrix elements (3.9) are determined with reference to the quasiparticle structure only; that is, using two-column (two-row) orbital (spin) tableau states [6,7].

For example, the spin-orbit interaction can be expressed alternatively as

$$V_{ee,\mathrm{SO}}=\sum_{\mu=1}^{N}\sum_{i=1}^{N_\mu}\tfrac{1}{2}g_s\mu_0\mathbf{S}_{\mu i}\cdot[\boldsymbol{\nabla}_{\mu i}U(\{\mathbf{r}_{\nu j}\})\times\boldsymbol{\nabla}_{\mu i}]$$

$$=\sum_{\mu=1}^{N}\sum_{i=1}^{N_\mu}g_s\mu_0\frac{f(r_{\mu i})}{r_{\mu i}^{3}}\mathbf{S}_{\mu i}\cdot\mathbf{L}_{\mu i}+(\text{small}) \tag{3.10a}$$

$$V_{nn,\mathrm{SO}}=\sum_{\mu=1}^{N}\frac{\tilde{f}(R_{\mu\nu})}{R_{\mu\nu}^{3}}\mathbf{S}_{\mu}\cdot\mathbf{V}_{\mu}^{(1)}\ , \tag{3.10b}$$

where the potential U is due to all fields except that of the (μi)th electron, g_s is the gyromagnetic ratio, μ_0 is the Bohr magneton, $f\,(\tilde{f}\,)$ accounts for the nonspherical symmetry of the charge distribution comprising the potential, **S** and **L** are the spin and orbital angular momentum operators and we assume that the spin-orbit interactions resulting from non-sphericity are small enough to neglect. Expression (3.10a) states the operator form applied to interacting electrons whereas (3.10b) is applied to quasi-particles using a pointlike approximation.

Matrix elements of the operator (3.10b) correspond to the case $\gamma_1=\gamma_2=\frac{1}{2}$ and $\Gamma=1$. Amendments to these matrix elements are then found directly from (3.7′)–(3.9).

The spin-spin interaction can be expressed in the alternative forms,

$$H_{\mathrm{SS}}=-\sum_{\mu=1}^{N-1}\sum_{\nu=\mu+1}^{N}\left\{J_0(R_{\mu\nu})\mathbf{S}_{\mu}\cdot\mathbf{S}_{\nu}-\sum_{i=1}^{N_\mu}\sum_{j=1}^{N_\nu}\frac{\xi(\rho_{\mu i,\nu j})}{\rho_{\mu i,\nu j}^{3}}\left[s_{\mu i}\cdot s_{\nu j}-\frac{3(\mathbf{s}_{\mu i}\cdot\boldsymbol{\rho}_{\mu i})(\mathbf{s}_{\nu j}\cdot\boldsymbol{\rho}_{\nu j})}{\rho_{\mu i,\nu j}^{2}}\right]\right\} \tag{3.11a}$$

$$\approx J_0S^{(0)}+\sum_{\mu=1}^{N-1}\sum_{\nu=\mu+1}^{N}g(R_{\mu\nu})\mathrm{c}^{(2)}(\mu,\nu)\cdot\mathrm{s}^{(2)}(\mu,\nu)\ , \tag{3.11b}$$

where $J_0(R_{\mu\nu})$ is the exchange integral and $\rho_{\mu i,\nu j}$ is the distance between the ith and jth electrons of the respective quasiparticles. $\mathrm{s}^{(2)}$ and $\mathrm{c}^{(2)}$ are second-rank tensor operators which act on spin and space, respectively. The expressions (3.11a) and (3.11b) refer to the operators applied to electrons versus quasiparticles, respectively.

The term involving $S^{(0)}$ is a scalar operator which acts to interchange spins of electrons i and j of quasiparticles μ and ν using (3.11a), or to interchange the spins of quasiparticles μ and ν using (3.11b). In either case, matrix elements are zero unless the quasiparticle states are from the same irrep. Furthermore, the matrix elements are zero, also, unless all orbital labels are identical except for position.

The second terms in (3.11a) and (3.11b) involve second-rank tensors which act independently on the orbital and spin states for an atomic wave function. Values for the $\mathrm{C}^{(2)}$ tensor are common in the literature [8]. The evaluation of the $S_Q^{(2)}$ tensor components is straightforward in cases where the single-atom spins are all $\frac{1}{2}$. These cases have been treated by Kent and co-workers [9] in the context of a spin-correlated system of electrons.

Matrix elements of (3.11b) are found by applying (3.7) with $\gamma_1=\gamma_2=1$ and $\Gamma=2$. In order to relate this expression to matrix elements of (3.11a) it is necessary to further express $\mathrm{s}^{(\gamma_1)}$ and $\mathrm{s}^{(\gamma_2)}$ as two-electron operators *and* approximate $\xi(\rho)/\rho^3$ by $g(R)$. The resulting amendment is, then, a product of Racah and 12-j symbols of the kind occurring in (3.7), one for each quasiparticle. Hence,

$$\langle(\Lambda';(\lambda'))\|S_{ee,[2],[2]}^{([4])}(\mu,\nu)\|(\Lambda;(\lambda))\rangle=\langle(\Lambda')\|S_{[2],[2]}^{([4])}(\mu,\nu)\|(\Lambda)\rangle\langle(\lambda'_\mu)\|S_{[1],[1]}^{([2])}\|(\lambda_\mu)\rangle\langle(\lambda'_\nu)\|S_{[1],[1]}^{([2])}\|(\lambda_\nu)\rangle\ , \tag{3.12}$$

where the operator indices [1], [2], and [4] are the partition labels for (symmetric) coupling of 1, 2, and 4 electrons corresponding to the single-electron ($\gamma=\frac{1}{2}$), triplet ($\gamma,\Gamma=1$), and quintet ($\Gamma=2$) coupling cases. The graph shown in Fig. 7 illustrates the coupling in this case.

To summarize the results of this section, we have derived algebraic expressions for the matrix elements of various tensor operators using the hierarchical basis functions. We have related those matrix element expressions based on the quasiparticle viewpoint to those found by taking into account the internal electronic structure. Finally, we note that the formalism, typical of the UGA, is extensible to any number of particles and ionic systems which is one of its main characteristics.

IV. CONCLUSIONS

We have shown how to construct hierarchical, permutation symmetry adapted basis functions, in the context

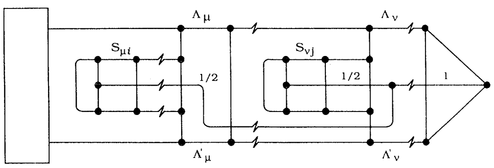


FIG. 6. Spin-graphical representation of reduced spin-orbit operator matrix element.

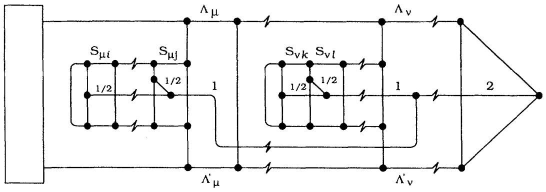


FIG. 7. Spin-graphical representation of reduced spin-spin operator matrix element.

of the unitary-group approach, which at once contain both a description of the electron ensemble about an ionic site treated as a quasiparticle and the detailed structure of the electron configuration. Using techniques developed previously these basis functions can be adapted to arbitrary space and spin symmetries.

We showed, furthermore, that matrix elements of spin-independent and spin-dependent quantum-mechanical tensor operators can be systematically and efficiently evaluated using the basis functions. In particular, the hierarchical nature of the basis functions allows for a simple means of determining the internal electronic "fine-structure" corrections to the matrix elements calculated using a strictly quasiparticle approach.

We anticipate that our approach and results will be of interest to those practitioners interested in the treatment of complex molecular or ligand systems. Our approach provides for a description of states which is intermediate between states defined using solely collective and local models. The advantages of this scheme should be realized in situations where the number of atomic species and states is relatively small, such as in some primitive lattice unit defined by an ion and its neighbors, and where detailed local interactions play a significant role.

Finally, readers interested in the mathematical details regarding phases and techniques for evaluating the various $3n$-j coefficients should consult Refs. [4] and [5].

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