Coordination chemistry in molecular symmetry adapted spin space (mSASS)

R. Matthias Geilhufe\textsuperscript{1,}\textsuperscript{*} and Jeffrey D. Rinehart\textsuperscript{2,}\textsuperscript{†}

\textsuperscript{1}Department of Physics, Chalmers University of Technology, Kemigården 1, 412 58 Göteborg, Sweden
\textsuperscript{2}Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California, USA

(Dated: September 8, 2022)

Many areas of chemistry are devoted to the challenge of understanding, predicting, and controlling the behavior of strongly localized electrons. Examples include molecular magnetism and luminescence, color centers in crystals, photochemistry and quantum sensing to name but a few. Over the years, an amalgam of powerful quantum chemistry methods, simple intuitive models, and phenomenological parameterizations have been developed, providing increasingly complex and specialized methodologies. Even with increasing specialization, a pervasive challenge remains that is surprisingly universal - the simultaneous description of continuous symmetries (e.g. spin and orbital angular momenta) and discrete symmetries (e.g. crystal field). Modeling and predicting behavior in these complex systems is increasingly important for metal ions of unusual or technologically relevant behavior. Additionally, development and adoption of broad-scope models with physically-meaningful parameters carries the potential to facilitate interdisciplinary collaboration and large-scale meta analysis. Here, we propose a generalized algorithmic approach, the molecular symmetry adapted spin space (mSASS), to localized electronic structure via descent directly from fermionic (spin) rather than bosonic (orbital) symmetry. We derive the Hamiltonian in symmetry-constrained matrix form with an exact account of free parameters and several usage examples. Although preliminary in its implementation, a fundamental benefit of this approach is the treatment of spatial and spin-orbit symmetries without the need for perturbative approximations. In general, the mSASS Hamiltonian is large but finite and can be diagonalized numerically with high efficiency, providing a basis for conceptual models of electronic structure that naturally incorporates spin while leveraging the intuition and efficiency benefits of crystallographic symmetry. For the generation of the mSASS Hamiltonian, we provide an implementation into the Mathematica Software Package, GTPack.

I. INTRODUCTION

Chemistry flourishes when synthetic efforts are driven by intuitive physical models that link structure to function. An iconic example from molecular chemistry is the control of the d-orbital manifold of transition metals via ligand coordination environment. In many cases, a surprising level of insight can be gained through the heuristic assumptions of a simplified symmetry and a basic electrostatic model (i.e. Crystal Field Theory; CFT) \[1\]-\[4\]. The limitations of CFT are often cited as evidence for involvement of ligand orbitals and thus the necessity of an expanded basis allowing for mixing with ligand orbitals (Ligand Field Theory; LFT) \[5\]. Indeed, benchmark structure-function relationships such as the spectrochemical series and nephelauxetic effect \[6\] require LFT insight \[7\]. Rightly so, the influence of ligand orbitals is considered foundational knowledge for many chemists. Knowledge of orbital moment and the spin-orbit interaction, however, is much less pervasive, despite being vital to understanding of electronic structure, especially for the d-orbital manifold of many materials of high physical and technological interest. Even though CFT/LFT models do not explicitly treat angular momentum, basic qualitative predictions can be made in simple cases with only the Pauli exclusion principle as a guide (e.g. spin-only models). Caution in this respect is imperative, however, as the underlying physics of electronic spin is absent here, limiting insight in both scope and scale.

Recognition of this issue goes back to the advent of quantum mechanics, and as disciplines became more specialized, approaches to the problem developed a dizzying array of formalisms. A common historic theme was that full spin quantum mechanical modeling or fitting was too computationally-intensive for practical use, and, in the end, unnecessary for empirical descriptions of most phenomena. For instance, exclusions of energy states outside of the range of interest vastly reduces the computational cost. Such simplifications trade physically meaningful operators for phenomenologically parameterized tensors to compensate for the simplified basis. Often referred to as spin Hamiltonians, \[8\]-\[11\], such models are particularly effective in efficiently reproducing magnetometry and magnetic spectroscopy data of transition metal complexes when the ground state lacks orbital angular momentum. Developed largely in the context of Electron Paramagnetic Resonance (EPR) \[12\], spin Hamiltonians are characterized by a lack of orbital operators with compensation via a phenomenological symmetry-restricted Hamiltonian acting directly on functions of the spin operators. There are a number of common methods for perturbations involving the orbital operators where the symmetry of the local crystal field is expanded into operator equivalents following methods of Stevens \[13\]-\[15\] or Buckmaster-Smith-Thornley \[16\], for example. This approach has proven powerful and efficient, in particular in situations of well-defined symmetry and low anisotropy.
While effective in fitting complex spectral data, there are reasons to consider alternative approaches to the crystal field expansion. The first of these reasons being the lack of intrinsic physical meaning to the parameters. Without the ability to generate falsifiable hypotheses for predicted spin state structure from coordination environment, progress towards new, overarching models or technological goals is drastically hindered. Additionally, many of the most exciting systems of current interest are incompatible with the spin Hamiltonian model. In cases of low-lying excited states and significant orbital moment, for example, employing a spin Hamiltonian will provide little insight. As a final point, somewhat counter-intuitively, a more complete incorporation of the underlying spin and orbital moment can actually reduce the overall complexity despite an expansion of the Hilbert space. The spin symmetry lost in the truncated basis can often be leveraged by modern computational algorithms to considerable effect. In this work, we present many of the most exciting systems of current interest are incompatible with the spin Hamiltonian model. Addition-

II. METHOD OVERVIEW

In the following section, we provide theoretical background outlining the molecular symmetry adapted spin space approach. To efficiently evaluate the symmetry constraints imposed on the crystal field Hamiltonian, we make use of the Mathematica group theory package GT-Pack [17, 18]. In particular, we extend the functionality of GT-Pack to calculate representation matrices of \( SU(2) \) and \( SU(2) \), as described throughout the main text and in the appendix. All examples presented here can be found in the Mathematica notebook format (Supporting information).

A. Spinor basis

The molecular symmetry adapted spin space (mSASS) method is constructed in the spinor basis (Fig. 1). For total angular momentum \( J \), a \((2J + 1)\)-dimensional basis is spanned by the functions \(|Jm\rangle\), with \( m = -J, \ldots, J \). For multiple values of \( J \), the basis is extended accordingly, \(|J, J_1 \rangle, |J_1, J_1 - 1 \rangle, \ldots, |J_1, -J_1 \rangle, |J_2, J_2 \rangle, |J_2, J_2 - 1 \rangle, \ldots, |J_2, -J_2 \rangle\).

B. Multi-electron basis

Many-particle basis functions are constructed in terms of direct products of single particle wave functions. For electrons, the wave function needs to satisfy fermionic statistics, i.e., being odd under particle-exchange. This constraint is satisfied by taking the alternating square of two representations, instead of the ordinary direct product [19].

In the following we introduce the characters of \( SU(2) \) representations and the construction of the alternating square. We start from rotation of angle \( \phi \) about the arbitrary axis \( n \), \( D^J(n, \phi) \), represented as

\[
D^J(n, \phi) = D^J(n', -\theta)D^J(e_z, \phi)D^J(n', \theta),
\]

with \( n' \) and \( \theta \) being the respective axis and angle to transform the initial axis \( n \) to the \( e_z \) axis. Due to the cyclic permutation rule for the trace operation we obtain for the characters \( \chi^J(n, \phi) \) and \( \chi^J(e_z, \phi) \),

\[
\chi^J(n, \phi) = \text{Tr} \left[ D^J(n', -\theta)D^J(e_z, \phi)D^J(n', \theta) \right],
\]

\[
\chi^J(e_z, \phi) = \text{Tr} \left[ D^J(n', \theta)D^J(n', -\theta)D^J(e_z, \phi) \right] = \text{Tr} \left[ D^J(e_z, \phi) \right] = \chi^J(e_z, \phi).
\]

Hence, without loss of generality, we focus on rotations about the \( z \)-axis in the following.

Since,

\[
D^J(e_z, \phi) = \exp \left( -iJ_z \phi \right) \quad \text{and} \quad \langle J, m|D^J(e_z, \phi)|J'm' \rangle = \delta_{mm'}\delta_{JJ'} \exp (-im'\phi) \quad \text{we obtain for the character}
\]

\[
\chi^J(e_z, \phi) = \sum_{m=-J}^J e^{-im\phi}.
\]

We continue by considering the direct product of two \( SU(2) \) representations, where we assume \( J_1 > J_2 \).

1) select relevant orbitals

2) construct N-electron multiplets

3) impose symmetry

4) project mSASS Hamiltonian

\[
\sum \left( \begin{array}{c}
\begin{array}{c}
\vdots
\end{array}
\end{array} \right) \left( \begin{array}{c}
\begin{array}{c}
\vdots
\end{array}
\end{array} \right)^{-2}
\]

FIG. 1: Outline of the molecular symmetry adapted spin space method.
$J_2$. By calculating the product $\chi^{J_1}(e_j, \phi)\chi^{J_2}(e_j, \phi) = \chi^{J_1+J_2}(e_j, \phi) + \chi^{J_1+J_2-1}(e_j, \phi) + \ldots + \chi^{J_1-J_2}(e_j, \phi)$ we obtain
\[ D^{J_1} \otimes D^{J_2} \simeq D^{J_1+J_2} \oplus D^{J_1+J_2-1} \oplus \ldots \oplus D^{J_1-J_2}. \] (3)

For $J_1 = J_2$, the representation matrices operate on the same finite vector space $V^J$. The basis of the direct product space $V^J \otimes V^J$ can be constructed from products $v_i v_j$, where $v_i, v_j \in V^J$ are a basis of $V^J$. This direct product can be decomposed into a symmetric (bosonic) and an antisymmetric (fermionic) part,
\[ V^J \otimes V^J = S(V^J \otimes V^J) \oplus A(V^J \otimes V^J). \] (4)

The symmetric and antisymmetric parts of the decomposition are also known as the symmetric and antisymmetric square of the representation. Correspondingly, one obtains for the direct product representation $D^J \otimes D^J \simeq D^2 \oplus D^A$ with $\chi^J(g) = \chi^{J}(g) + \chi^{A}(g)$. The respective characters for the symmetric and the antisymmetric square are [19],
\[
\chi^{S}(g) = \frac{1}{2} (\chi^{J}(g^2) + \chi^{J}(g^2)) ,
\]
\[
\chi^{A}(g) = \frac{1}{2} (\chi^{J}(g^2) - \chi^{J}(g^2)) ,
\]
where $g \in G$ is a symmetry element of the group $G$.

Finally, we give the decomposition of the antisymmetric square in terms of representations of $SU(2)$,
\[
A(D^J \otimes D^J) \simeq D^{2J-1} \oplus D^{2J-3} \oplus \ldots \oplus D^0 . \] (7)

The above equation can be obtained from applying (5) to equation (6).
As an example, we consider $J = \frac{1}{2}$ and the well known direct product
\[ D^{1/2} \otimes D^{1/2} \simeq D^1 \oplus D^0 . \] (8)

From equation (7) it follows that the antisymmetric part of the direct product is given by the spin-singlet $D^0$,
\[ A(D^{1/2} \otimes D^{1/2}) \simeq D^0 . \] (9)

The respective results for all direct products involving single values of $J_i$ relevant for $s-f$ electrons with and without spin orbit coupling are given in Table I.

C. Construction of the mSASS Hamiltonian

Consider a system with a basis belonging to several total angular momenta $J_i$, where each $J_i$ corresponds to a $(2J_i + 1)$-dimensional subspace with basis function $u_{m}^{J_i}$ ($J_i \geq m \geq -J_i$). Furthermore, consider a crystal field with symmetry group $G$. By definition, the transformation of $u_{m}^{J_i}$ under a symmetry element $g \in G$ is given by
\[ g u_{m}^{J_i} = \sum_{m'} (-J_i) D^{J_i}_{m' m} (g) u_{m'}^{J_i} , \] (10)

with $D^{J_i}_{m' m} (g)$ denoting the matrix of the irreducible representation of SO(3) corresponding to $J_i$. In general, $D^{J_i}_{m' m} (g)$ form a reducible representation in $G \subset SO(3)$.

The total dimension of a Hamiltonian spanned by $(u_{1}^{J_1}, u_{-1}^{J_1}, \ldots, u_{1}^{J_2}, \ldots)$ is given by
\[ d = \sum_{i} (2J_i + 1) . \] (11)

The corresponding Hamiltonian is a $d \times d$-dimensional matrix [20],
\[ \tilde{H} = \begin{pmatrix} h_{11} & h_{12} & \ldots & h_{1d} \\ h_{21} & h_{22} & \ldots & h_{2d} \\ \vdots & \vdots & \ddots & \vdots \\ h_{1d} & h_{2d} & \ldots & h_{dd} \end{pmatrix} . \] (12)

This matrix has to be invariant under all symmetry elements of $G$, imposing
\[ \tilde{H} = \sum_{g \in G} \tilde{D}(g) \tilde{H} \tilde{D}(g)^{-1} , \] (13)

where $\tilde{D}(g)$ denotes the super representation of $g$ incorporating all matrices $\tilde{D}^{J_i}(g)$ as follows,
\[ \tilde{D}(g) = \begin{pmatrix} \tilde{D}^{J_1}(g) & 0 & \ldots & 0 \\ 0 & \tilde{D}^{J_2}(g) & \ldots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \ldots & \tilde{D}^{J_n}(g) \end{pmatrix} . \] (14)

While $\tilde{H}$ is diagonal in blocks belonging to different $J_i$, imposing [13] for $G \subset SO(3)$ separates $\tilde{H}$ into blocks belonging to different irreducible representations of $G$. The diagonal formulation of $\tilde{H}$ in terms of $J_i$ represents the unrestricted rotational symmetry of the chosen angular momentum operators. If multiple types of angular momenta are used (e.g. $J = S+L$) intra-$J_i$ coupling terms naturally incorporate any associated interactions.

TABLE I: The antisymmetric squares for relevant direct products arising for $s-f$ electrons with and without spin-orbit coupling

| $A(D^{1/2} \otimes D^{1/2}) \simeq D^0$ | $A(D^1 \otimes D^1) \simeq D^1$ |
| $A(D^{3/2} \otimes D^{3/2}) \simeq D^2 \oplus D^0$ | $A(D^2 \otimes D^2) \simeq D^2 \oplus D^1$ |
| $A(D^{5/2} \otimes D^{5/2}) \simeq D^4 \oplus D^2 \oplus D^0$ | $A(D^3 \otimes D^3) \simeq D^4 \oplus D^2 \oplus D^1$ |
| $A(D^{7/2} \otimes D^{7/2}) \simeq D^5 \oplus D^4 \oplus D^2 \oplus D^0$ |
via symmetry (e.g. the spin-orbit interaction). When the further constraint of $G \subset SO(3)$ is included, (13) inter-$J$ terms arise naturally from the symmetry of $G$ to account for the new crystal field interactions. Due to the symmetry constraints of real molecules, $D^{J_i}$ can now be reduced in $G$ to give

$$D^{J_i} \sim n_1 \Gamma^1 \oplus n_2 \Gamma^2 \oplus \cdots \oplus n_n \Gamma^n,$$

(15)

where $\Gamma^i$ are the $n$ nonequivalent irreducible representations of $G$. Hence, in the most general form, the mSASS Hamiltonian $\hat{H}$ is given by

$$\hat{H} = \begin{pmatrix}
\bar{H}_{\Gamma_1,1} & \bar{h}_1 & \cdots & 0 & \cdots & \Delta_1 & \cdots \\
\bar{h}_1 & \bar{H}_{\Gamma_1,2} & \cdots & 0 & \cdots & \Delta_2 & \cdots \\
\vdots & \vdots & \ddots & \vdots & \ddots & \vdots & \ddots \\
0 & 0 & \cdots & \bar{H}_{\Gamma_n,0} & \cdots & 0 & \cdots \\
\vdots & \vdots & \ddots & \vdots & \ddots & \vdots & \ddots \\
\Delta_1 & \Delta_1 & \cdots & 0 & \cdots & \bar{H}_{\Gamma_1, \beta} & \cdots \\
\vdots & \vdots & \ddots & \vdots & \ddots & \vdots & \ddots
\end{pmatrix}$$

(16)

Here $\bar{h}_i$ ($\Delta_i$) are intra-hybridization (inter-hybridization) coupling terms belonging to equivalent irreducible representations $\Gamma^i$ of $G$, but the same (different) $J$. The implementation of this formalism is shown below in several cases where pre-existing intuition will be helpful. In this work, we do not yet apply the method in complex or quantitative methods, instead focusing on establishing the groundwork for further development and implementation. As an aid in this process, the mSASS Hamiltonian $\hat{H}$ can be derived from evaluating equation (13) using the Mathematica Software Package, GTPack. (17) (18)

III. EXAMPLES

To evaluate equation (13) for specific point group symmetries $g \in G$, we implemented a new module GTAngularMomentumRep into the Mathematica group theory package GTPack (17) (18), calculating the $SU(2)$ and $SO(3)$ representation matrices $D^J(g)$. Full details of the implementation are given in the appendix and software documentation. Briefly, the starting point for implementation of orbital symmetry is often $O(3)$, the full roto-reflection group of $\mathbb{R}^3$ represented by orthonormal $3 \times 3$ matrices of det $= \pm 1$). $O(3)$ is the direct product of $SO(3)$ and the group $S_I = \{E, I\}$ ($E$ the identity, $I$ the inversion). $O(3) = SO(3) \times S_I$. The irreducible representations of $O(3)$ come as even and odd variants. The physically relevant representations are even (odd) under inversion for even (odd) angular momenta $l$. Hence, for $d$-electrons, the corresponding irreducible representation of $O(3)$ would be $D_2^2$.

A. The $d^1$ configuration in an octahedral crystal field

To introduce the methodology, we will build up the textbook example of a single $d$-electron in an octahedral, $O$, crystal field where spin is not a factor outside of the Pauli exclusion principle. In Section III.B, we will add detail through the introduction of spinor representations, constructing the fermionic picture in the presence of simultaneous symmetry restrictions of the spin-orbit and crystal field interactions.

Considering only the orbital moment, the five-fold degenerate $d$-electron wave function in $O$-symmetry splits according to

$$D^2 \simeq E \oplus T_2.$$

(17)

Note that we choose $O$ for our analysis of the restrictions of the crystal field rather than the inversion symmetric $O_h$. The pure rotational octahedral group, $O$, provides a more straightforward example, as well as one of more general utility due to the ready extension to the tetrahedral case, $T$.

In terms of real (tesseral) spherical harmonics $Y_m^l = \langle r|l, m\rangle$, the basis of the 5-dimensional subspace belonging to $l = 2$ is given by

$$\{2, 2, |2, 1\rangle, |2, 0\rangle, |2, -1\rangle, |2, -2\rangle\}.$$ (18)

In this basis, the mSASS Hamiltonian matrix is diagonal, giving rise to three-fold degenerate ($T_2$) and two-fold degenerate ($E$) electronic configurations,

$$\hat{H} = \begin{pmatrix}
\epsilon_E & 0 & 0 & 0 & 0 \\
0 & \epsilon_{T_2} & 0 & 0 & 0 \\
0 & 0 & \epsilon_E & 0 & 0 \\
0 & 0 & 0 & \epsilon_{T_2} & 0 \\
0 & 0 & 0 & 0 & \epsilon_{T_2}
\end{pmatrix}.$$ (19)

To refer to the general form of the mSASS Hamiltonian in (16), we note that the matrices $\hat{H}_E$ and $\hat{H}_{T_2}$ are diagonal, i.e., $\hat{H}_E = \text{diag} (\epsilon_E, \epsilon_E)$ and $\hat{H}_{T_2} = \text{diag} (\epsilon_{T_2}, \epsilon_{T_2}, \epsilon_{T_2})$. As each representation only occurs once, the coupling matrices vanish, $\bar{h}_i = \Delta_i = 0$. The eigenfunctions of the mSASS Hamiltonian for a $d^1$ configuration in an octahedral field can be constructed to transform as

$$\Psi_{T_2:1} \sim \langle r|2, 1\rangle \sim xz,$$ (20)

$$\Psi_{T_2:2} \sim \langle r|2, -1\rangle \sim yz,$$ (21)

$$\Psi_{T_2:3} \sim \langle r|2, -2\rangle \sim xy,$$ (22)

$$\Psi_{E:1} \sim \langle r|2, 0\rangle \sim z^2 - r^2,$$ (23)

$$\Psi_{E:2} \sim \langle r|2, 2\rangle \sim x^2 - y^2.$$ (24)

Note that in the case of a single electron, these eigenfunctions have the mathematical form of the commonly used Cartesian $d$-orbital set. It is important, however, not to conflate the solutions to (10) (corresponding to possible configurations available to a $d^1$ electron count) with...
the concept of orbital energy levels. The corresponding Mathematica code can be found in the supplemental material.

Throughout this work we focus mainly on the cubic symmetry $O$ as a representative example. Without modification, however, the algorithm used for $O$ may be applied to any point group symmetry. For example, the degeneracy of possible configurations for $d^1$ may be lowered from $O$ to $D_4$ by an axial Jahn-Teller distortion, leading to symmetry lowering according to:

$$E \simeq A_1 \oplus B_1, \quad (25)$$

$$T_2 \simeq E + B_2. \quad (26)$$

In agreement with this decomposition, the mSASS Hamiltonian is of the form

$$\hat{H} = \begin{pmatrix}
\epsilon_{B_1} & 0 & 0 & 0 & 0 \\
0 & \epsilon_E & 0 & 0 & 0 \\
0 & 0 & \epsilon_{A_1} & 0 & 0 \\
0 & 0 & 0 & \epsilon_E & 0 \\
0 & 0 & 0 & 0 & \epsilon_{B_2}
\end{pmatrix}. \quad (27)$$

The corresponding eigenfunctions of the mSASS Hamiltonian for the $d^1$ configuration in square symmetry transform as follows

$$\Psi_{E;1} \sim \langle r|2, 1 \rangle \sim xz, \quad (28)$$

$$\Psi_{E;2} \sim \langle r|2, -1 \rangle \sim yz, \quad (29)$$

$$\Psi_{B_2} \sim \langle r|2, -2 \rangle \sim xy, \quad (30)$$

$$\Psi_{A_1} \sim \langle r|2, 0 \rangle \sim z^2 - r^2, \quad (31)$$

$$\Psi_{B_1} \sim \langle r|2, 2 \rangle \sim x^2 - y^2. \quad (32)$$

A schematic of the hierarchical symmetry lowering of the $d$-state by $O$ and $D_4$ crystal fields is shown in Fig. 3.

B. The $d^1$ configuration in an octahedral crystal field with spin-orbit coupling

Orbital symmetry has been argued as the greatest driver of intuitive models for chemical synthesis, properties, and reactivity in the era of modern quantum theory: spin-symmetry, on the other hand, has had only minor influence. While the reasons for this are complex and beyond the scope of this work, in many ways the triage of spin can be attributed to the search for configuration subspaces accessible by contemporary computational methods. These subspaces, though vastly reduced in dimensionality, lack the overarching symmetry restrictions of the original space. When applied to systems with non-trivial spin interactions, the reduced space may still effectively emulate the properties of the local region of the full space assuming the subspace remains largely orthogonal to the full configuration space (i.e. cases where interactions arising from spin comprise only very minor perturbations on the energy). In the framework of (16), $\Delta_s \approx 0$.

Because of the limitations of the restricted subspace to minor perturbations, the spin-orbit interaction is typically discussed in terms of two limits. In the first limit, the spin-orbit interaction dominates the crystal field, causing a splitting of the $d$-level into two levels with angular momenta $j = 3/2$ and $j = 5/2$. These levels then split in the presence of the crystal field. Continuing from our example of $O$ symmetry, the splitting follows

$$D^{3/2} \simeq F_{3/2}, \quad (33)$$

$$D^{5/2} \simeq E_{5/2} \oplus F_{3/2}. \quad (34)$$

The far more common case in valence electrons of chemical importance occurs when the crystal field dominates. Here, one can discuss the splitting of the $E$ and $T_2$ levels discussed previously, due to spin orbit interaction. In the case of the group $O$, these representations split as follows

$$E \simeq F_{3/2}, \quad (35)$$

$$T_2 \simeq E_{5/2} \oplus F_{3/2}. \quad (36)$$

In general, however, the two levels transforming as $F_{3/2}$...
interact. To obtain the corresponding mSASS Hamiltonian, we constrain the problem to the 10-dimensional subspace containing spinor functions belonging to the angular momenta \( j_1 = 3/2 \) and \( j_2 = 5/2 \),
\[
\{ |3/2,3/2 \rangle, \ldots, |3/2,-3/2 \rangle, |5/2,5/2 \rangle, \ldots, |5/2,-5/2 \rangle \} .
\] (37)

The corresponding super representation \([14]\) is given by the Clebsch-Gordan sum
\[
D = D^{3/2} \oplus D^{5/2} .
\] (38)

As there are two equivalent representations \( (F_{3/2}) \) and one additional representation \( (E_{5/2}) \), we expect four free parameters in our theory, three determining the three levels, plus one parameter determining the interaction between the levels belonging to the equivalent representation \( F_{5/2} \). Evaluating \([13]\), our algorithm gives the following mSASS Hamiltonian matrix for \( d^1 \) configurations under the full spin-orbit symmetry, with the parameters \( \lambda_1, \ldots, \lambda_4 \),
\[
\bar{H} = \begin{pmatrix}
\lambda_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \lambda_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \lambda_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \lambda_2 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -\sqrt{5}\lambda_4 & \lambda_1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \lambda_2 & -\sqrt{5}\lambda_4 & 0 & 0 & 0 & 0 \\
\lambda_4^* & 0 & 0 & 0 & 0 & 0 & \lambda_3 & 0 & 0 & 0 \\
0 & -\sqrt{6}\lambda_4 & 0 & 0 & 0 & 0 & 0 & \lambda_3 & 0 & 0 \\
0 & 0 & \sqrt{6}\lambda_4^* & 0 & 0 & 0 & 0 & 0 & \lambda_3 & 0 \\
0 & 0 & 0 & -\lambda_4^* & \lambda_3 & 0 & 0 & 0 & 0 & 0 \\
0 & \sqrt{5}\lambda_4^* & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
\] (39)

By diagonalizing the matrix, one of the four parameters can be seen to represent the absolute energy scale and set to zero or an arbitrary offset. For real-valued parameters, the resulting energies for each term can be expressed as follows,
\[
\epsilon_{E_{5/2}} = \lambda_2 - \sqrt{5}\lambda_3 \quad (40)
\]
\[
\epsilon_{F_{3/2,1}} = a - b, \quad (41)
\]
\[
\epsilon_{F_{3/2,2}} = a + b, \quad (42)
\]
with
\[
a = \frac{1}{2} \left( \lambda_1 + \lambda_2 + \frac{1}{\sqrt{5}} \lambda_3 \right) , \quad (43)
\]
\[
b = \sqrt{a^2 - \lambda_1 (a - \lambda_1) + 6\lambda_4^2}. \quad (44)
\]
The corresponding eigenvectors are parameter dependent and are expressed as a linear combination of the basis functions given in \([17]\). As the eigenvectors transform as irreducible representations retaining the full spinor symmetry, they can be used to form a symmetry-restricted model of the full configuration space as a function of the full parameter space. Such models can provide useful insight on the often opaque intermediate configuration space away from the strong crystal field or spin-orbit limits. Additionally, the use of the symmetry restricted full configuration space allows for a more physically-meaningful model for fitting spin-dependent data. This flows from the fact that a given physical measurement often represents only a fraction of the energy range needed to parameterize a complex electronic structure. If the model is constructed for the energy range of the measurement instead of the energy range of the physical parameters, the relationship between the fitted parameters and the “true” ones is ill-defined and generally not useful for comparison across different systems.

### C. Continuous symmetry parameterization of multielectronic configurations

In the last example, we provide a simple extension to the multielectron case: a \( p^1 \) configuration within an octahedral field. This case extends the coordination chemistry examples used so far and serves as a demonstration of the versatility offered by taking a wider view of electronic structure problems. Configurations of several \( p \)-electrons occur e.g., in color centers or vacancies, and play an important role in \( d^1 \)- magnetism \([21, 22]\) and NV centers \([23, 24]\). For simplicity, we focus on two electrons in the \( p_{3/2} \)-state, assuming that the \( p_{1/2} \) state is fully occupied and sufficiently separated in energy from \( p_{3/2} \). The corresponding alternating square from Tab. 1 is
\[
A \left( D^{3/2} \oplus D^{5/2} \right) \sim D^2 \oplus D^0 . \quad (45)
\]
As before, we choose a basis in terms of angular momentum states. However, here we need to consider 2-electron wave functions,
\[
|J, M_J; j_1 j_2 \rangle = \{|2, 2; 3/2 \rangle, \ldots, |2, -2; 3/2 \rangle, |0, 0; 3/2 \rangle \} . \quad (46)
\]
which are constructed using Clebsch-Gordan coefficients and the addition of angular momenta,

$$|2, 2; \frac{3}{2}\rangle = \frac{1}{\sqrt{2}} (|\frac{3}{2}\rangle - |\frac{1}{2}\rangle - |\frac{1}{2}\rangle)$$, 

(47)

$$|2, 1; \frac{3}{2}\rangle = \frac{1}{\sqrt{2}} (|\frac{3}{2}\rangle - |\frac{1}{2}\rangle - |\frac{1}{2}\rangle)$$, 

(48)

$$|2, 0; \frac{3}{2}\rangle = \frac{1}{\sqrt{2}} (|\frac{3}{2}\rangle + |\frac{1}{2}\rangle - |\frac{1}{2}\rangle)$$, 

(49)

$$|2, -1; \frac{3}{2}\rangle = \frac{1}{\sqrt{2}} (|\frac{3}{2}\rangle - |\frac{1}{2}\rangle - |\frac{1}{2}\rangle)$$, 

(50)

$$|2, -2; \frac{3}{2}\rangle = \frac{1}{\sqrt{2}} (|\frac{3}{2}\rangle - |\frac{1}{2}\rangle - |\frac{1}{2}\rangle)$$, 

(51)

$$|0, 0; \frac{3}{2}\rangle = \frac{1}{\sqrt{2}} (|\frac{3}{2}\rangle - |\frac{1}{2}\rangle - |\frac{1}{2}\rangle)$$, 

(52)

In $O$ symmetry, the representations $D^2$ and $D^0$ are decomposed as before,

$$D^2 \simeq E \oplus T_2, \quad D^0 \simeq A_1.$$ 

(53)

In contrast to the single $d$-electron Hamiltonian in [19], we choose a complex valued representation according to our basis in [46]. Applying equation (13) as before, we obtain a mSASS Hamiltonian with 3 free parameters,

$$\hat{H} = \begin{pmatrix}
\lambda_1 & 0 & 0 & 0 & \lambda_3 & 0 \\
0 & \lambda_1 - \lambda_3 & 0 & 0 & 0 & 0 \\
0 & 0 & \lambda_1 + \lambda_3 & 0 & 0 & 0 \\
0 & 0 & 0 & \lambda_1 - \lambda_3 & 0 & 0 \\
\lambda_3 & 0 & 0 & 0 & \lambda_1 & 0 \\
0 & 0 & 0 & 0 & \lambda_2 & 0
\end{pmatrix}. $$

(54)

The eigenvalues of this Hamiltonian are the level energies

$$\epsilon_{T_2} = \lambda_1 - \lambda_3, \quad \epsilon_E = \lambda_1 + \lambda_3, \quad \epsilon_{A_1} = \lambda_2.$$ 

(55, 56, 57)

The eigenvectors of the Hamiltonian in terms of the respective two-electron basis functions are given by

$$\Psi_{T_2;1} \sim |2, 1; \frac{3}{2}\rangle, $$

(58)

$$\Psi_{T_2;2} \sim \frac{1}{\sqrt{2}} (|2, -2; \frac{3}{2}\rangle - |2, 2; \frac{3}{2}\rangle), $$

(59)

$$\Psi_{T_2;3} \sim |2, -1; \frac{3}{2}\rangle, $$

(60)

$$\Psi_{E;1} \sim |2, 0; \frac{3}{2}\rangle, $$

(61)

$$\Psi_{E;2} \sim \frac{1}{\sqrt{2}} (|2, -2; \frac{3}{2}\rangle + |2, 2; \frac{3}{2}\rangle), $$

(62)

$$\Psi_{A_1} \sim |0, 0; \frac{3}{2}\rangle. $$

(63)

As can be seen, the $T_2$ state corresponds to a spin-triplet with $J = 1$, whereas the levels $E$ and $A_1$ give rise to spin singlets with $J = 0$. The result is summarized in Fig. 4

IV. CONCLUSION

Ideally, computational modeling, synthesis, and physical characterization of spin physics in molecular species would all fall under an overarching, universal framework robust enough to allow scientists to communicate through everything from back-of-the-envelope to supercomputer computations.

The molecular symmetry adapted spin space (mSASS) method allows for a generalization of the crystal field theory for calculating atomic spectra, taking into account the mixing of levels with different angular momenta, when exposed to a symmetry breaking molecular environment. The mSASS Hamiltonian is constructed by, first, fixing a subspace consisting of several angular momentum multiplets belonging to a central atom or cluster, and, second, imposing symmetry constraints of the molecular environment. We outlined the approach on three simple examples, the $d^1$ configuration in octahedral and square symmetry, the $d^1$ configuration in octahedral symmetry with spin-orbit interaction, and, the $p^2$ configuration in an octahedral field.

By way of introduction, we have provided a case for the need, theoretical basis, and simple implementation of the method, leaving detailed exploration of specific applications and fitting to experiments for subsequent work. These works will include, for example, symmetry-adapted splitting of states in a magnetic field.

We close by providing one more advantage of the mSASS method, compared to conventional crystal field theory. Note, that evaluating (13) is generic. By lifting the Hermiticity of the mSASS Hamiltonian, the method can be generalized towards open quantum systems, i.e., quantum systems interacting with a thermal bath [27, 29]. In such systems, electrons occupying certain levels decay in time, which is a natural description for excited local electrons. A non-Hermitian mSASS Hamiltonian contains the respective decay channels in terms of gen-
erally complex parameters. As such, it might play a powerful role, e.g., in optimizing the coherence time of molecular qubits [30] by symmetry principles.

**AUTHOR CONTRIBUTIONS**

All authors contributed equally. RMG implemented the necessary algorithms into the Mathematica group theory package GTPack.

**CONFLICTS OF INTEREST**

There are no conflicts to declare.

**ACKNOWLEDGEMENTS**

We thank Wolfram Hergert for helpful discussions. RMG acknowledges support from Chalmers University of Technology. JDR acknowledges the National Science Foundation Division of Chemistry CHE-2154830.

**APPENDIX**

Irreducible representation of SU(2)

In the process of the present work, a new module GTAngularMomentumRep was implemented into the Mathematica group theory package GTPack [17]18, calculating the SU(2) and SO(3) representation matrices. We follow the approach derived by Altmann [31]. Note that the SU(2) matrices represent the \( j = 1/2 \) representation of SU(2). We obtain all other representations by constructing corresponding tensor products as described below. As SU(2) is the double cover of SO(3), all SO(3) representations are obtained in terms of integer valued \( j \). The \( j = 1/2 \) representation is spanned by two basis functions \( \mu_{-1/2} \) and \( \mu_{1/2} \), such that

\[
\hat{g} \mu_1 = \sum_{j=-1/2}^{1/2} \hat{R}_{ji}(g) \mu_j.
\] (64)

The basis can be used to construct tensors \( \mu_{ijk\ldots} = \mu_{i} \mu_{j} \mu_{k} \ldots \), transforming as

\[
\hat{g} \mu_{ijk\ldots} = \sum_{IJK\ldots} \hat{R}_{Ii}(g) \hat{R}_{Jj}(g) \hat{R}_{Kk}(g) \ldots \mu_{IJK\ldots}. \] (65)

We constrain ourselves to focus on the totally symmetric tensors having the property \( \mu_{i\ldots mn\ldots} = \mu_{i\ldots nm\ldots} \), i.e., they are symmetric with respect to pairwise permutation of indices. Hence, we can order indices such that all values \(-1/2\) are listed on the left and all \(1/2\) on the right. This construction can be abbreviated by a function \( v^j_m \) as follows

\[
v^j_m = \mu_{-1/2} \mu_{-1/2} \ldots \mu_{1/2} \mu_{1/2} \ldots = \mu_{-m} \mu_{j+m}. \] (66)

Acting on \( v^j_m \) with the angular momentum operator \( \hat{J}_z \) gives

\[
\hat{J}_z v^j_m = \left( - (j - m) \frac{1}{2} + (j + m) \frac{1}{2} \right) v^j_m = m v^j_m. \] (67)

Note that \( \hat{J}_z \) acts like a differential operator, i.e.,

\[
\hat{J}_z \mu_{m_1} \mu_{m_2} = \left( \hat{J}_z \mu_{m_1} \right) \mu_{m_2} + \mu_{m_1} \left( \hat{J}_z \mu_{m_2} \right). \] Normalizing \( v^j_m \) leads to the final form

\[
v^j_m = \frac{1}{(j + m)!(j - m)!} \mu^{j-m} \mu^{j+m}. \] (68)

The representation matrices for higher \( j \) can now be deduced by acting on the normalized \( v^j_m \). A general transformation using SU(2) matrices for \( j = 1/2 \) can be written as

\[
\left( \begin{array}{cc} \alpha & b \\ b^* & a \end{array} \right) \left( \begin{array}{c} \mu_{-1/2} \\ \mu_{1/2} \end{array} \right) = \left( \begin{array}{c} \alpha \mu_{-1/2} - b^{*} \mu_{1/2} \\ b \mu_{-1/2} + a^{*} \mu_{1/2} \end{array} \right). \] (69)

Using (68) we therefore obtain

\[
\hat{g} v^j_m = \frac{1}{(j + m)!(j - m)!} \left( \begin{array}{c} \alpha \mu_{-1/2} - b^{*} \mu_{1/2} \\ b \mu_{-1/2} + a^{*} \mu_{1/2} \end{array} \right) \mu^{j-m} \mu^{j+m} \] (70)

This expression can be expanded using the binomial theorem, giving

\[
\hat{g} v^j_m = \frac{1}{(j + m)!(j - m)!} \left( \begin{array}{c} \alpha^{j-m} \mu_{-1/2} - b^{*j-m} \mu_{1/2} \\ b^{j-m} \mu_{-1/2} + a^{j-m} \mu_{1/2} \end{array} \right). \] (71)

Rewriting the indices as \( 2j - k - \kappa = j + m' \) and \( k + \kappa = j - m' \) and noting that \( j - k \leq m' \leq j - k \), leads to the final equation

\[
\hat{g} v^j_m = c^{j}_{mm'} \sum_{m'-j-k}^{m+j} \sum_{k=0}^{m-j-m} (j + m)!(j - m - \kappa)! \kappa! \times a^{j-m-k} b^{j-m-\kappa} (a^{*})^{j-k-\kappa} \mu^{j-m-k} \mu^{j+m+\kappa}. \] (72)

with

\[
c^{j}_{mm'} = (j + m)!(j - m)!(j + m')!(j - m')! \frac{1}{1/2}. \] (73)

Equation (72) is used to determine the representation matrices \( D^j(g) \), which satisfy

\[
\hat{g} v^j_m = \sum_{m'=-j}^j D^j_{m'm}(g) v^j_{m'}. \] (74)
The limits where either \( a = 0 \) or \( b = 0 \) can be derived straightforwardly from (71) without using the binomial series.

### Character Tables

The character tables are calculated using a Burnside algorithm, implemented in GTPack. We choose the Mulliken notation for the irreducible representations \([32, 33]\), as tabulated by Altmann and Herzig \([34]\). Representations under the separation are double group representations (see \([18]\) for more information).

| \( E \) | \( 3C_2 \) | \( 8C_3 \) | \( 6C_4 \) | \( 6C'_2 \) |
|---|---|---|---|---|
| \( A_1 \) | 1 | 1 | 1 | 1 |
| \( A_2 \) | 1 | 1 | -1 | -1 |
| \( E \) | 2 | 2 | -1 | 0 |
| \( T_1 \) | 3 | -1 | 0 | 1 |
| \( T_2 \) | 3 | -1 | 0 | -1 |

| \( E \) | \( 2C_4 \) | \( C_2 \) | \( 2C'_2 \) | \( 2C''_2 \) |
|---|---|---|---|---|
| \( A_1 \) | 1 | 1 | 1 | 1 |
| \( A_2 \) | 1 | 1 | -1 | -1 |
| \( B_1 \) | 1 | -1 | 1 | -1 |
| \( B_2 \) | 1 | -1 | -1 | 1 |
| \( E \) | 2 | 0 | -2 | 0 |

### References

[1] H. Bethe, Termalopaltung in kristallen, Annalen der Physik 395, 133 (1929).
[2] O. Danielsen and P.-A. Lindgård, Quantum mechanical operator equivalents used in the theory of magnetism, 259 (Jul. Gjellerup, 1972).
[3] J. Mulak and Z. Gajek, The effective crystal field potential (Elsevier, 1972).
[4] J.-L. Liu, Y.-C. Chen, and M.-L. Tong, Symmetry strategies for high performance lanthanide-based single-molecule magnets, Chemical Society Reviews 47, 2431 (2018).
[5] J. Griffith and L. Orgel, Ligand-field theory, Quarterly Reviews, Chemical Society 11, 381 (1957).
[6] C. K. Jørgensen, The nephelauxetic series, in Progress in Inorganic Chemistry (John Wiley & Sons, Ltd, 1962) pp. 73–124.
[7] C. K. Jørgensen, Recent progress in ligand field theory, Structure and Bonding, 3 (1966).
[8] X. Li, H. Yu, F. Lou, J. Feng, M.-H. Whangbo, and H. Xiang, Spin hamiltonians in magnets: Theories and computations, Molecules, 26, 803 (2021).
[9] C. Rudowicz and M. Karboviak, Disentangling intricate web of interrelated notions at the interface between the physical (crystal field) hamiltonians and the effective (spin) hamiltonians, Coordination Chemistry Reviews 287, 28 (2015).
[10] M. Mostafanejad, Basics of the spin hamiltonian formalism, International Journal of Quantum Chemistry 114, 1495 (2014).
[11] S. Misra, A review of spin hamiltonians applicable to exchange-coupled systems of interest in biomaterials, Applied Magnetic Resonance 24, 127 (2003).
[12] A. Abragam and B. Bleaney, Electron paramagnetic resonance of transition ions (Oxford University Press, 2012).
[13] K. Stevens, Matrix elements and operator equivalents connected with the magnetic properties of rare earth ions, Proceedings of the Physical Society. Section A 65, 209 (1952).
[14] I. Ryabov, On the generation of operator equivalents and the calculation of their matrix elements, Journal of Magnetic Resonance 140, 141 (1999).
[15] C. Rudowicz and C. Chung, The generalization of the extended stevens operators to higher ranks and spins, and a systematic review of the tables of the tensor operators and their matrix elements, Journal of Physics: Condensed Matter 16, 5825 (2004).
[16] D. Smith and J. Thornley, The use of operator equivalents, Proceedings of the Physical Society 89, 779 (1966).
[17] R. M. Geilhufe and W. Hergert, GTPack: A Mathematical Group Theory Package for Application in Solid-State Physics and Photonics, Frontiers in Physics 6, 86 (2018).
[18] W. Hergert and R. M. Geilhufe, Group Theory in Solid State Physics and Photonics: Problem Solving with Mathematica (Wiley-VCH, 2018) ISBN: 978-3-527-41133-7.
[19] G. James, M. W. Liebeck, and M. Liebeck, Representations and characters of groups (Cambridge University Press, 2001).
[20] We note that a Hermitian matrix was historically chosen to enforce real eigenvalues of the Hamiltonian. This condition can be lifted towards PT-symmetric matrices \([35]\) which bring a new twist to quantum chemistry. Also, non-Hermitian matrices are meaningful, in the context of open quantum systems \([29]\).
[21] J. Coey, Magnetism in d0 oxides, Nature Materials 18, 652 (2019).
[22] P. Esquinazi, W. Hergert, D. Spemann, A. Setzer, and A. Ernst, Defect-induced magnetism in solids, IEEE Transactions on Magnetics 49, 4668 (2013).
[23] G. m. H. Thiering and A. Gali, Ab initio calculation of spin-orbit coupling for an nv center in diamond exhibiting dynamic jahn-teller effect, Physical Review B 96, 081115 (2017).
[24] A. Gali, M. Fyta, and E. Kaxiras, Ab initio supercell calculations on nitrogen-vacancy center in diamond: Electronic structure and hyperfine tensors, Physical Review B 77, 155206 (2008).
[25] N. B. Manson, J. P. Harrison, and M. J. Sellars, Nitrogen-vacancy center in diamond: Model of the electronic structure and associated dynamics, Physical Review B 74, 104303 (2006).
[26] A. Lenef and S. C. Rand, Electronic structure of the n-v center in diamond: Theory, Physical Review B 53, 13441 (1996).
[27] C. P. Koch, Controlling open quantum systems: tools, achievements, and limitations, Journal of Physics: Con-
densed Matter 28, 213001 (2016).

[28] I. Rotter and J. Bird, A review of progress in the physics of open quantum systems: theory and experiment, Reports on Progress in Physics 78, 114001 (2015).

[29] I. Rotter, A non-hermitian hamilton operator and the physics of open quantum systems, Journal of Physics A: Mathematical and Theoretical 42, 153001 (2009).

[30] A. Gaita-Ariño, F. Luis, S. Hill, and E. Coronado, Molecular spins for quantum computation, Nature chemistry 11, 301 (2019).

[31] S. L. Altmann, *Rotations, quaternions, and double groups* (Courier Corporation, 2005).

[32] (empty), Report on notation for the spectra of polyatomic molecules, The Journal of Chemical Physics 23, 1997 (1955).

[33] R. S. Mulliken, Erratum : Report on notation for the spectra of polyatomic molecules, The Journal of Chemical Physics 24, 1118 (1956).

[34] S. Altmann and P. Herzig, *Point-group theory tables*, Oxford science publications (Clarendon Press, 1994).

[35] C. M. Bender, S. Boettcher, and P. N. Meisinger, Ptsymmetric quantum mechanics, Journal of Mathematical Physics 40, 2201 (1999).