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Efficient Algorithm for Many-Electron Angular Momentum and Spin Diagonalization on Atomic Subshells

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Abstract. We devise an efficient algorithm for the symbolic calculation of irreducible angular momentum and spin (LS) eigenspaces within the n-fold antisymmetrized tensor product $\wedge^n V_u$, where n is the number of electrons and $u = \mathrm{s,p,d,}\cdots$ denotes the atomic subshell. This is an essential step for dimension reduction in configuration-interaction (CI) methods applied to atomic many-electron quantum systems. The algorithm relies on the observation that each L_z eigenstate with maximal eigenvalue is also an $\boldsymbol{L}^2$ eigenstate (equivalently for S_z and $\boldsymbol{S}^2$), as well as the traversal of LS eigenstates using the lowering operators L_- and S_-. Iterative application to the remaining states in $\wedge^n V_u$ leads to an *implicit* simultaneous diagonalization. A detailed complexity analysis for fixed n and increasing subshell number u yields run time $\mathcal{O}(u^{3n-2})$. A symbolic computer algebra implementation is available online.

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Key words: Angular momentum and spin symmetry, atomic many-electron quantum systems, symbolic computation.

1 Introduction

Since the inception of quantum mechanics, it is well-known that the (non-relativistic, Born-Oppenheimer) Hamiltonian governing many-electron atoms leaves the simultaneous eigenspaces of the angular momentum, spin and parity (LS) operators

$$\boldsymbol{L}^2,\ L_z,\ \boldsymbol{S}^2,\ S_z,\ \hat{R} \tag{1.1}$$

invariant. From a practical perspective, the restriction to symmetry subspaces can significantly reduce computational costs (see, e.g., Refs. [1–4]). In particular, such a restriction

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is an essential ingredient for configuration interaction (CI) approximation methods in Refs. [5–7]. However, simultaneous diagonalization of the operators (1.1) on the full CI space is encumbered by the inherent "curse of dimensionality", which renders "naive" $\mathcal{O}(\dim^3)$ approaches infeasible. The present paper outlines an efficient algorithm for computing the symbolic eigenspaces by making use of representation theory and the algebraic properties of the LS operators.

In (1.1), the total angular momentum operator is defined as $\boldsymbol{L}=\sum_{j=1}^n \boldsymbol{L}(j)$ with n the number of electrons and

$$\boldsymbol{L}(j)=\tfrac{1}{\mathbb{i}}\boldsymbol{x}_j\times\boldsymbol{\nabla}_j \tag{1.2}$$

the angular momentum operator acting on electron j. (We choose units such that $\hbar=1$.) L_z is the third component of $\boldsymbol{L}$. In spherical polar coordinates, $L_z(j)=\frac{1}{\mathbb{i}}\partial/\partial\varphi_j$. Analogously for spin, $\boldsymbol{S}=\sum_{j=1}^n \boldsymbol{S}(j)$ with $S_\alpha(j)$ for $\alpha=x,y,z$ the usual Pauli matrices

$$\sigma_x=\frac{1}{2}\begin{pmatrix}0&1\\1&0\end{pmatrix},\quad \sigma_y=\frac{1}{2}\begin{pmatrix}0&-\mathbb{i}\\\mathbb{i}&0\end{pmatrix},\quad \sigma_z=\frac{1}{2}\begin{pmatrix}1&0\\0&-1\end{pmatrix} \tag{1.3}$$

acting on electron j. The components of the angular and spin operators obey the well-known commutator relations $[L_\alpha,L_\beta]=\mathbb{i}L_\gamma$ and $[S_\alpha,S_\beta]=\mathbb{i}S_\gamma$ with α,β,γ cyclic permutations of x,y,z. The *ladder operators* are given by $L_\pm=L_x\pm\mathbb{i}L_y$ and $S_\pm=S_x\pm\mathbb{i}S_y$. They have the property that for any angular momentum eigenfunction ψ^{m_ℓ} with eigenvalue m_ℓ, $L_\pm\psi^{m_\ell}$ is zero or an eigenfunction with eigenvalue $m_\ell\pm1$, and correspondingly for spin. The *parity operator* acts on wavefunctions as $\hat{R}\psi(\boldsymbol{x}_1,s_1,\cdots,\boldsymbol{x}_n,s_n)=\psi(-\boldsymbol{x}_1,s_1,\cdots,-\boldsymbol{x}_n,s_n)$, where $\boldsymbol{x}_j\in\mathbb{R}^3$ and $s_j\in\{-\frac{1}{2},\frac{1}{2}\}$ are the position and spin coordinate of electron j.

The simultaneous diagonalization of the LS operators is greatly simplified by representation theory using Clebsch-Gordan coefficients. Specifically, the required computational cost is reduced to the calculation of irreducible LS representation spaces (i.e., diagonalizing the operators (1.1)) on the n-fold antisymmetrized tensor product $\wedge^n V_u$ (compare with Ref. [7, proposition 2]). Here, V_u denotes an angular momentum subshell, $u=\mathrm{s,p,d,f},\cdots$ in chemist's notation. An explicit realization of V_u is

$$V_u=\mathrm{span}\{Y_{u,m}\uparrow,Y_{u,m}\downarrow\}_{m=u,u-1,\cdots,-u} \tag{1.4}$$

with the spherical harmonics $Y_{u,m}$:

$$\begin{gathered}Y_{\mathrm{s},0}=\tfrac{1}{\sqrt{4\pi}},\\ Y_{\mathrm{p},1}=-\tfrac{1}{2}\sqrt{\tfrac{3}{2\pi}}\sin(\theta)\mathrm{e}^{\mathbb{i}\varphi},\quad Y_{\mathrm{p},0}=\tfrac{1}{2}\sqrt{\tfrac{3}{\pi}}\cos(\theta),\quad Y_{\mathrm{p},-1}=\tfrac{1}{2}\sqrt{\tfrac{3}{2\pi}}\sin(\theta)\mathrm{e}^{-\mathbb{i}\varphi}\\ \cdots\end{gathered}$$

We identify the subshell label u with the corresponding quantum number, i.e., $\mathrm{s,p,d,f},\cdots\leftrightarrow 0,1,2,3,\cdots$. In particular, $\dim(V_u)=2(2u+1)$. Note that $Y_{u,m}\uparrow$, $Y_{u,m}\downarrow$ are simultaneous single-particle L_z-S_z eigenstates. They serve as underlying ordered orbitals, which we