Spin Projection made easy

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The use of projected wavefunctions has gained attention in recent years, from the original work of Scuseria et al. [1], by providing a Projected Hartree-Fock theory, several extensions of the method have appeared. Especially promising is the application to post-PHF methods, like to single and double excitations in the CI method [2]. In all these applications the projected wavefunction is attained by expressing the projector operator in integral form and performing a numerical integration over a gauge angle.
In the present work [3] we propose to use the Löwdin projector, this is a clear (and robust) way to recover the spin symmetry of a UHF determinant, $\widehat{\mathcal{P}_S}\,|\Psi_{\text{UHF}}\rangle = \sum_k C_k(S)\,|T_k\rangle$. However, its naive application is not computationally feasible, since it requires considering all spin-flipped determinants. To overcome this difficulty, we show that introducing a formal parameter, that collection can be recast into a single determinant. The fundamental result states that the sum T_k of all determinants with k spin-flips corresponds to the coefficients of the following polynomial

$$\sum_k \langle \Psi_{\text{UHF}}\,|\,T_k\rangle\, z^{\nu-k} = \begin{vmatrix} \mathbb{I}_\mu & \mathbf{S} \\ \mathbf{S}^\dagger & z\cdot\mathbb{I}_\nu \end{vmatrix}, \tag{1}$$

where $S_{ij} = \langle\phi_i|\theta_j\rangle$, i.e. the overlaps between *up* and *down* spatial orbitals. This result is used to derive compact expressions for operator matrix elements over spin projected wavefunctions, resulting in a *Projection After Variation* scheme where the projection is carried out exactly, removing all spin contaminants. It is suitable in cases when the reference determinant has contaminants of many different spins. This procedure could be considered as an alternative to the more general method of *Analytic Energy Gradients* applied to the projection of $\hat{S}^2$ [4]. Having expressed the combination of determinants as a single entity permits to optimize the orbitals by requiring them to minimize the projected energy, leading to a Pople-Nesbet alike system of equations. The application of the formalism to the CI method has been also considered.
We apply our results to circularly confined quantum dots, and (possibly) under the influence of a magnetic field. In such systems, spin symmetry, as well as rotational symmetry restoration methods have proved to be a valuable technique [5]. To allow for a simultaneous restoration of the circular symmetry the method has been extended. We show how the (spatial-) RHF method fails to predict the L_z and S_z quantum numbers of the ground states for a large region of the magnetic field strength and Wigner parameter (measure of the relative strength between electron-electron interaction and confinement). While the quantum numbers from projecting broken symmetry determinants agree quite well with the prediction of Full CI calculations.

References

1. G. Escuseria, *J. Chem. Phys.* **136** (2012), 164109.
2. T. Tsuchimochi and S. Ten-no, *J. Chem. Theory Comput.* (2016), 1741.
3. M. Pons Viver, *Int. J. Quantum Chem.* **119** (2019), e25770.
4. M. Uejima and S. Ten-no, *J. Chem. Phys.* **146** (2017), 104106.
5. C. Yannouleas and U. Landman, *Rep. Prog. Phys.* **70**, (2007), 2067.