On the permutation symmetry of atomic and molecular wavefunctions

Francisco M. Fernández *
INIFTA, División Química Teórica
Blvd. 113 S/N, Sucursal 4, Casilla de Correo 16,
1900 La Plata, Argentina

Abstract

In this paper we analyze a recently proposed approach for the construction of antisymmetric functions for atomic and molecular systems. It is based on the assumption that the main problems with Hartree-Fock wavefunctions stem from their lack of proper permutation symmetry. This alternative building approach is based on products of a space times a spin function with opposite permutation symmetry. The main argument for devising such factors is that the eigenfunctions of the non-relativistic Hamiltonian are either symmetric or antisymmetric with respect to the transposition of the variables of a pair of electrons. However, since the eigenfunctions of the non-relativistic Hamiltonian are basis for the irreducible representations of the symmetric group they are not necessarily symmetric or antisymmetric, except in the trivial case of two electrons. We carry out a simple and straightforward general analysis of the symmetry of the eigenfunctions of the non-relativistic Hamiltonian and illustrate our conclusions by means of two exactly-solvable models of \( N = 2 \) and \( N = 3 \) identical interacting particles.

*E-mail: fernande@quimica.unlp.edu.ar
1 Introduction

It is well known that the application of quantum mechanics to systems of identical particles requires taking into account the permutation symmetry of the Hamiltonian operator \[1\]. The postulates of quantum mechanics state that the wavefunctions that describe Bosons or Fermions should be symmetric or antisymmetric, respectively, with respect to the transposition of the variables of identical particles \[1\]. For this reason, the solutions to the Schrödinger equation for atomic and molecular systems are commonly approximated by Slater determinants that are antisymmetric functions constructed from monoelectronic spin-orbitals \[2\]. This way of constructing the variational functions leads to the Hartree-Fock (HF) method and its variants \[2\]. Besides, it is well known that the Slater determinants are consistent with Pauli exclusion principle \[2\].

In a recent paper Nascimento \[3\] argues that the main problems exhibited by the HF approximate wavefunctions stem from the fact that they do not actually take into account the proper permutation symmetry of the non-relativistic atomic and molecular Hamiltonians. He proposes that alternative better functions should be the product of a space function times a spin one with opposite permutation symmetry, namely, symmetric×antisymmetric or antisymmetric×symmetric. According to the author this more suitable approach is based on the fact that each exact eigenfunction \(\psi_{el}\) of the non-relativistic electronic Hamiltonian \(H_{el}\) satisfies \(P_{ij}\psi_{el} = \pm \psi_{el}\) \(\forall i, j\), where \(P_{ij}\) is a permutation (transposition \[1\]) operator for a pair of particle labels \(i\) and \(j\). The author argues that the better results derived from the Generalized Valence Bond (GVB) Method with respect to HF comes precisely from the fact that the former takes into account true permutation symmetry while the latter does not.

The purpose of this paper is to analyze the validity of the argument based on the permutation symmetry of \(\psi_{el}\) just mentioned. In section \[2\] we outline the main ideas about the application of permutation groups to atomic and molecular systems. In section \[3\] we illustrate the general results by means of two exactly-solvable models for \(N = 2\) and \(N = 3\) identical interacting particles. Finally, In
section we summarize the main results, add some further comments and draw conclusions.

2 Permutation symmetry

The non-relativistic Hamiltonian $H$ of an $N$-electron system is invariant under the transposition $P_{ij}$ of any pair of electron variables. For this reason the commutator between both operators vanishes: $[H, P_{ij}] = 0$. Since any permutation of the electron labels can be written as a product of a finite number of transpositions we focus on the latter. However, we must keep in mind that the symmetric group $S_N$ consists of $N!$ permutation operators of which $N(N - 1)/2$ are transpositions.

If $\psi$ is an eigenfunction of $H$ with eigenvalue $E$ then the obvious equalities $P_{ij}H\psi = HP_{ij}\psi = EP_{ij}\psi$ tell us that $P_{ij}\psi$ is also an eigenfunction of $H$ with eigenvalue $E$. If the energy level $E$ is non-degenerate then $P_{ij}\psi = \lambda\psi$, where $\lambda$ is a constant. Since $P_{ij}^2$ is the identity operator then $\lambda = \pm 1$ and $\psi$ is either symmetric or antisymmetric under the permutation of the pair $i, j$ of electron coordinates. However, if the energy level is degenerate, then $P_{ij}\psi$ and $\psi$ are not necessarily linearly dependent and we cannot assure that $P_{ij}\psi = \pm\psi$.

The question is if it is possible to find linear combinations of the degenerate eigenfunctions that are either symmetric or antisymmetric. In what follows we will show that the answer is negative for most of them.

In the case of two electrons we can find a set of eigenfunctions common to $H$ and $P_{12}$ and, consequently, we are certain that all the eigenfunctions of $H$ can be chosen to be either symmetric or antisymmetric. However, when $N > 2$ the transposition operators do not commute $[P_{ij}, P_{kl}] \neq 0$ and we cannot obtain eigenfunctions common to $H$ and all the transposition operators. In the next section we will show an exactly-solvable example that illustrates these points.

In the case of three particles the equations

$$P_{12}P_{13}f(r_1, r_2, r_3) = P_{12}f(r_3, r_2, r_1) = f(r_3, r_1, r_2),$$
\[ P_{12}P_{13}f(r_1, r_2, r_3) = P_{13}f(r_2, r_1, r_3) = f(r_2, r_3, r_1), \] (1)

clearly show that \( P_{12} \) and \( P_{13} \) do not commute. If we choose \( \psi \) to be eigenfunction of both \( H \) and \( P_{12} \) it will not be necessarily eigenfunction of \( P_{13} \) or \( P_{23} \).

The symmetric group \( S_3 \) for three identical particles is isomorphic to the point groups \( D_3 \) and \( C_{3v} \) commonly used in the description of the symmetry of molecular states in quantum-chemistry calculations based on the Born-Oppenheimer approximation \([2]\). The three irreducible representations are labelled \( A_1, A_2 \) and \( E \) \([4]\) (the construction of the character table for the symmetric group \( S_3 \) can be seen in https://groupprops.subwiki.org/wiki/Determination\(_{\text{of}}\)\_character\(_{\text{table}}\)\(_{\text{of}}\)\_symmetric\(_{\text{group}}\):\( S_3 \)). We can use the character table of \( C_{3v} \) to obtain the basis functions for the irreducible representations by straightforward application of the projection operators \( P_S \) \([4]\) to an arbitrary function \( f(r_1, r_2, r_3) \). For example:

\[
\begin{align*}
 f_{A_1}(r_1, r_2, r_3) &= P_{A_1}f(r_1, r_2, r_3) = \frac{1}{6} [f(r_1, r_2, r_3) + f(r_3, r_2, r_1) + f(r_1, r_3, r_2) &+ f(r_2, r_1, r_3) + f(r_3, r_1, r_2) + f(r_2, r_3, r_1)] , \\
 f_{A_2}(r_1, r_2, r_3) &= P_{A_2}f(r_1, r_2, r_3) = \frac{1}{6} [f(r_1, r_2, r_3) + f(r_3, r_2, r_1) + f(r_1, r_3, r_2) &- f(r_2, r_1, r_3) - f(r_3, r_1, r_2) - f(r_2, r_3, r_1)] , \\
 f_{E_1}(r_1, r_2, r_3) &= P_{E_1}f(r_1, r_2, r_3) = \frac{1}{3} [2f(r_1, r_2, r_3) - f(r_2, r_3, r_1) - f(r_3, r_1, r_2)] , \\
 f_{E_2}(r_1, r_2, r_3) &= P_{E_2}f(r_2, r_1, r_3) = \frac{1}{3} [2f(r_2, r_1, r_3) - f(r_1, r_3, r_2) - f(r_3, r_2, r_1)] , \\
 f_{E_3}(r_1, r_2, r_3) &= P_{E_3}f(r_3, r_1, r_2) = \frac{1}{3} [2f(r_3, r_1, r_2) - f(r_1, r_2, r_3) - f(r_2, r_3, r_1)] , \\
 f_{E_4}(r_1, r_2, r_3) &= P_{E_4}f(r_1, r_3, r_2) = \frac{1}{3} [2f(r_1, r_3, r_2) - f(r_2, r_1, r_3) - f(r_3, r_2, r_1)] .
\end{align*}
\]

We clearly see that from the six functions derived from all the permutations of the variables of \( f(r_1, r_2, r_3) \) we obtain one of symmetry \( A_1 \), one of symmetry \( A_2 \) and two pairs of symmetry \( E \). One can easily verify that \( P_{ij}f_{A_1} = f_{A_1} \), \( P_{ij}f_{A_2} = -f_{A_2} \) and \( P_{ij}f_{E_i} \neq \pm f_{E_i} \). We cannot derive symmetric or antisymmetric functions from linear combinations of \( f_{E_1}, f_{E_2}, f_{E_3} \) and \( f_{E_4} \) because
$P_{A_1}f_{E_i} = P_{A_2}f_{E_i} = 0$. The conclusion is that the eigenfunctions of $H$ having symmetry $E$ will not be eigenfunctions of all the transposition operators which contradicts Nascimento’s assumption that $P_{ij}\psi = \pm \psi$ for any eigenfunction $\psi$ of $H$. We will illustrate these points in section 3. It should be taken into account that the six symmetry-adapted functions just discussed are nonzero provided that the functions obtained by the six permutations of the three arguments of $f(r_1, r_2, r_3)$ are linearly independent.

The situation is even worse for systems of more particles; for example, $S_4$ is isomorphic to $O$ or $T_d$ (see also https://groupprops.subwiki.org/wiki/Linear_representation_theory_of_symmetric_group:S4) and we have the irreducible representations $A_1$, $A_2$, $E$, $T_1$ and $T_2$, so that only the functions that are basis for $A_1$ and $A_2$ are eigenfunctions of all the transposition operators. In this case we cannot obtain symmetric or antisymmetric functions from linear combinations of the basis functions for the remaining irreducible representations $E$, $T_1$ and $T_2$.

The full molecular Hamiltonian (which includes the kinetic energy of nuclei) is invariant under permutation of the variables of the electrons and also of identical nuclei. Both the atomic and full molecular Hamiltonians are also invariant under parity $Pf(r_1, r_2, \ldots) = f(-r_1, -r_2, \ldots)$. Since $[H, P] = 0$ and $[P, P_{ij}] = 0$ then all the eigenstates of $H$ satisfy $P\psi = \pm \psi$; that is to say, they are either even or odd.

### 3 Exactly-solvable models

In the case of atoms and molecules one cannot solve the Schrödinger equation exactly and, consequently, one is restricted to apply the results outlined above to the approximate wavefunctions that one commonly uses to describe the physical properties of such systems. However, there are many simple toy models that are exactly solvable and exhibit the desired permutation symmetry. In what follows, we illustrate the main ideas of the preceding section by means of two such examples.
3.1 $N = 2$ toy model

The simple two-particle model

$$H = -\frac{1}{2} \left( \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} \right) + \frac{1}{2} (x_1^2 + x_2^2) + \xi x_1 x_2,$$

(3)

clearly exhibits permutation symmetry in addition to parity invariance (exactly like the Hamiltonian of a two-electron system). The advantage of this model is that the Schrödinger equation is exactly solvable. In fact, by means of the change of variables

$$x_1 = \frac{1}{\sqrt{2}} (y_1 + y_2) \quad x_2 = \frac{1}{\sqrt{2}} (y_2 - y_1),$$

$$y_1 = \frac{1}{\sqrt{2}} (x_1 - x_2) \quad y_2 = \frac{1}{\sqrt{2}} (x_1 + x_2),$$

(4)

the Hamiltonian becomes

$$H = -\frac{1}{2} \left( \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial y_2^2} \right) + \frac{1}{2} \left[ (1 - \xi) y_1^2 + (1 + \xi) y_2^2 \right].$$

(5)

We appreciate that there are bound states when $-1 < \xi < 1$. The corresponding eigenfunctions and eigenvalues are given by

$$\psi_{n_1 n_2}(x_1, x_2) = N_{n_1 n_2} H_{n_1} \left[ (1 - \xi)^{1/4} y_1 \right] H_{n_2} \left[ (1 + \xi)^{1/4} y_2 \right] \times \exp \left[ -\frac{\sqrt{(1 - \xi)}}{2} y_1^2 + \frac{\sqrt{(1 + \xi)}}{2} y_2^2 \right],$$

$$E_{n_1 n_2} = \sqrt{(1 - \xi)} \left( n_1 + \frac{1}{2} \right) + \sqrt{(1 + \xi)} \left( n_2 + \frac{1}{2} \right), \quad n_1, n_2 = 0, 1, \ldots,$$

(6)

where $N_{n_1 n_2}$ is a suitable normalization factor that is not relevant for present purposes and $H_n(q)$ is a Hermite polynomial. Since $P_{12} y_1 = -y_1$ and $P_{12} y_2 = y_2$ we conclude that every eigenfunction is either symmetric or antisymmetric: $P_{12} \psi_{n_1 n_2}(x_1, x_2) = (-1)^{n_1} \psi_{n_1 n_2}(x_1, x_2)$. Also note that $P \psi_{n_1 n_2}(x_1, x_2) = \psi_{n_1 n_2}(-x_1, -x_2) = (-1)^{n_1 + n_2} \psi_{n_1 n_2}(x_1, x_2)$ as argued in the preceding section.

In this case it is possible to obtain antisymmetric wavefunctions of the form $\psi_{\text{space}} \psi_{\text{spin}}$ for all the eigenfunctions $\psi_{n_1 n_2}$ of the non-relativistic Hamiltonian.
If $\psi_{\text{space}}$ is symmetric, then $\psi_{\text{spin}}$ is antisymmetric and one obtains a singlet state. If, on the other hand, $\psi_{\text{space}}$ is antisymmetric, then we have three symmetric spin functions and the resulting products give rise to a triplet. Nascimento [3] chose only two-electron examples to illustrate his proposal and therefore his conclusions appeared to be sound.

3.2 $N = 3$ toy model

The Hamiltonian

$$H = -\frac{1}{2} \left( \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} \right) + \frac{1}{2} \left( x_1^2 + x_2^2 + x_3^2 \right) + \xi (x_1 x_2 + x_1 x_3 + x_2 x_3),$$

(7)

exhibits $S_3$ permutation symmetry and is parity invariant. It can be exactly solved by means of the change of variables

\begin{align*}
x_1 &= \frac{\sqrt{2} y_2}{3} + \frac{\sqrt{3} y_3}{3}, \\
x_2 &= \frac{\sqrt{6} y_1}{2} - \frac{\sqrt{6} y_2}{6} + \frac{\sqrt{3} y_3}{3}, \\
x_3 &= - \frac{\sqrt{2} y_1}{2} - \frac{\sqrt{2} y_3}{2} - \frac{\sqrt{6} y_2}{6} + \frac{\sqrt{3} y_3}{3},
\end{align*}

(8)

that leads to

$$H = -\frac{1}{2} \left( \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial y_3^2} \right) + \frac{1 - \xi}{2} (y_1^2 + y_2^2) + \frac{1 + 2 \xi}{2} y_3^2.$$  

(9)

We appreciate that there are bound states provided that $-1/2 < \xi < 1$. Under this condition the eigenfunctions and eigenvalues are given by

$$\psi_{n_1, n_2, n_3}(x_1, x_2, x_3) = N_{n_1, n_2, n_3} H_{n_1} \left( [1 - \xi]^{1/4} y_1 \right) H_{n_2} \left( [1 - \xi]^{1/4} y_2 \right) \times H_{n_3} \left( [1 + 2 \xi]^{1/4} y_3 \right) \times \exp \left[ -\frac{\sqrt{(1 - \xi)}}{2} (y_1^2 + y_2^2) - \frac{\sqrt{(1 + 2 \xi)}}{2} y_3^2 \right].$$

$$E_{n_1, n_2, n_3} = \sqrt{(1 - \xi) (n_1 + n_2 + 1) + \sqrt{(1 + 2 \xi)} \left( n_3 + \frac{1}{2} \right)},$$

$$n_1, n_2, n_3 = 0, 1, 2, \ldots.$$  

(10)

Since $y_1^2 + y_2^2$ and $y_3^2$ are invariant under permutation, then the symmetry of an eigenfunction is determined by the product of the three Hermite polynomials.
Thus, the ground state is symmetric as expected. The excited non-degenerate state $\psi_{001}$ is also symmetric. On the other hand, the 2-fold degenerate states $\psi_{100}$ and $\psi_{010}$ are neither symmetric nor antisymmetric and it is not difficult to convince oneself that there are no linear combinations of $y_1$ and $y_2$ that are simultaneous eigenfunctions of the three transposition operators $P_{ij}$. The reason is that these variables are basis functions for the irreducible representation $E$ while the symmetric and antisymmetric functions are basis for $A_1$ and $A_2$, respectively, as argued above. Therefore, $P_{A_1} \psi_{100} = 0$ and $P_{A_1} \psi_{010} = 0$.

Since $P_y y_j = -y_j$ then $P \psi_{n_1,n_2,n_3}(x_1,x_2,x_3) = \psi_{n_1,n_2,n_3}(-x_1,-x_2,-x_3) = (-1)^{n_1+n_2+n_3} \psi_{n_1,n_2,n_3}(x_1,x_2,x_3)$ in agreement with the result of section 2.

In this case it is not possible to construct antisymmetric functions of the form $\psi_{s\text{pace}} \psi_{s\text{pin}}$ for all the states. First, if $\psi_{s\text{pace}}$ is basis for the irreducible representation $E$ it is neither symmetric nor antisymmetric. Second, if $\psi_{s\text{pace}}$ is basis for $A_1$ we cannot construct a three-electron antisymmetric spin function (see below). The only case in which we can obtain antisymmetric functions of the form $\psi_{s\text{pace}} \psi_{s\text{pin}}$ is when $\psi_{s\text{pace}}$ is basis for $A_2$ and $\psi_{s\text{pin}} = \omega(s_1) \omega(s_2) \omega(s_3)$ with $\omega$ being either $\alpha$ or $\beta$ (the one-electron spin functions for $m_s = 1/2$ or $m_s = -1/2$, respectively).

According to the principles of quantum mechanics the states of the system should be basis for $A_2$. We can obtain such states by forcing the antisymmetry on products of space times spin functions; for example by means of the expression $P_{A_2} \psi_{n_1,n_2,n_3}(x_1,x_2,x_3) \omega_i(s_1) \omega_j(s_2) \omega_k(s_3) = \psi_{n_1,n_2,n_3}(x_1,x_2,x_3) P_{A_2} \omega_i(s_1) \omega_j(s_2) \omega_k(s_3) = 0$. The symmetric spatial functions, one of those proposed by Nascimento [2], are not allowed by the principles of quantum mechanics. Furthermore, a configuration interaction calculation based on a linear combination of suitable Slater determinants will not give the energy levels $E_{00n}$ because the corresponding eigenfunctions $\psi_{00n}$ are basis for the irreducible representation $A_1$.

It is worth noting that the conclusion just drawn applies to any realistic three-dimensional $N$-electron model because the argument is based only on
the permutation of the variables in the wavefunction and is, therefore, model independent (the irreducible representation $A_1$ appears in any symmetric group $S_N$).

4 Further comments and conclusions

In the preceding two sections we have clearly shown that the eigenfunctions $\psi$ of a non-relativistic Hamiltonian $H$ for a system of $N > 2$ identical particles do not satisfy $P_{ij}\psi = \pm \psi$ for all $i,j$ and all $\psi$. There are always two one-dimensional irreducible representations of $S_N$ that satisfy this requirement but the basis for the remaining representations are neither symmetric nor antisymmetric. For this reason it is not possible to construct antisymmetric functions of the form $\psi_{\text{space}}\psi_{\text{spin}}$ except for the states with $|M_S| = \max\{S\}$. Nascimento [3] considered only two-electron examples where such factorization is possible for all states because there is only one transposition operator and $S_2$ exhibits only two one-dimensional irreducible representations, the basis of which are symmetric and antisymmetric functions.

Permutation symmetry is a well-defined mathematical concept. In the case of $N = 2$ particles the operators $S = \frac{1}{2}(1 + P_{12})$ and $A = \frac{1}{2}(1 - P_{12})$ project onto the spaces of symmetric and antisymmetric functions, respectively [1]. For example: $S\phi_1(1)\phi_2(2) = \frac{1}{2} [\phi_1(1)\phi_2(2) + \phi_2(1)\phi_1(2)]$, $A\phi_1(1)\phi_2(2) = \frac{1}{2} [\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2)]$, $S\phi(1)\phi(2) = \phi(1)\phi(2)$ and $A\phi(1)\phi(2) = 0$. Therefore, from a strictly mathematical point of view $\phi(1)\phi(2)$ is a well-defined symmetric function [1]. Curiously, Nascimento [3] considers the permutation operator to be ill-defined in the latter case, a statement that obviously has no mathematical support.

In the case of helium-like atoms we may obtain a reasonable approximation to the ground state by means of an approximate trial function of the form $\varphi(\eta) = 1S(\eta r_1)1S(\eta r_2)$, where $1S$ is a hydrogen-like atomic orbital and $\eta$ an effective nuclear charge to be optimized by means of the variational method [2]. Eckart [5] proposed the trial function $\varphi(\alpha, \beta) = 1S(\alpha r_1)1S(\beta r_2) + 1S(\beta r_1)1S(\alpha r_2)$ that is obviously better because it has two adjustable parameters and reduces to the
when $\alpha = \beta$. Consequently, it is not surprising that the latter yields a lower, and therefore better, energy than the former. From a strict mathematical point of view both functions are symmetric because $P_{12}\varphi = \varphi$. In this case, variational flexibility and not lack of permutation symmetry (as argued by Nascimento) is the cause of the different performances.

We can carry out a similar analysis of the comparison of molecular orbital and valence bond methods in the case of the ground-state of the hydrogen molecule in the Born-Oppenheimer approximation. Both approximate space functions are symmetric under permutation of the electrons but the valence bond function was constructed to yield the exact result in the dissociation limit [2]. It is therefore no surprising its striking better performance at large internuclear distances. Once again, the lack of permutation symmetry invoked by Nascimento does not appear to be the issue.

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