Allowed permutation symmetry in atomic and molecular wavefunctions. Simple examples

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Abstract

It is well known that the allowed wavefunctions for an N-electron system should be antisymmetric with respect to the permutation of any pair of electron labels. On the other hand, the Hamiltonian for such system is invariant under any permutation of electron labels and, consequently, its eigenfunctions are basis for the irreducible representations of the symmetric group S_N . Here, we investigate which symmetry species of the S_N group are compatible with the antisymmetry principle. We illustrate the conclusions by means of simple N-particle one-dimensional models with harmonic interactions.

1 Introduction

There has recently been a controversy about the permutation symmetry of atomic and molecular Hamiltonians and the approaches commonly used to obtain their eigenvalues and eigenfunctions. On one hand it has been stated that Hartree-Fock and related methods do not take into account the permutation

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symmetry of the non-relativistic Hamiltonian, which "leads to false concepts, misinterpretations and unjustifiable approximations when dealing with manyelectron systems" [1]. On the other hand, it has been shown that the arguments put forward in that paper violate well known mathematical theorems and that the analysis is based on an incorrect application of the permutation operators of the symmetric group S_N [2]. Such interesting discussion motivated the analysis of the permutation symmetry of electronic systems carried out below in this paper.

The postulates of quantum mechanics state that the wavefunction for a system of particles should be symmetric or antisymmetric under the permutation of the variables of identical particles if they are either bosons or fermions, respectively. In the particular case of an N-electron system the wavefunction should be antisymmetric with respect to the transposition of the coordinates of any pair of electrons. For this reason approximate calculations of the electronic structure of atoms and molecules is commonly based on Slater determinants constructed from suitably chosen spin-orbitals. The configuration interaction (CI) method is known to provide accurate atomic and molecular electronic energies [3]. On the other hand, it is well known that the non-relativistic Hamiltonian for a system of N electrons is invariant under the N! permutations of the electronic variables. For this reason its eigenfunctions are basis for the irreducible representations (irreps) of the symmetric group S_N . Since the Schrödinger equation for an N-electron system is not exactly solvable for N > 1 there are no available comparisons between the exact solutions of the non-relativistic system and sufficiently accurate results provided by widely used methods like CI, except for some exactly-solvable models [4]. It would be interesting, for example, to know to which non-relativistic energy levels converges a CI calculation based on a Slater-determinant basis set.

The purpose of this paper is to fill this gap by means of exactly-solvable non-relativistic models with S_N symmetry that can be easily treated by means of CI to a great degree of accuracy. In section 2 we outline the concepts of permutation symmetry that are relevant for present discussion. In section 3 we

solve the Schrödinger equation for a simple non-relativistic model with N=3 identical particles. In section 4 we carry out a similar analysis for N=4. Finally, in section 5 we summarize the main results and draw conclusions.

2 Permutation symmetry

The Hamiltonian operator H for an N-electron system is invariant under the transposition P_{ij} of the variables of any pair of electrons i,j; that is to say: $P_{ij}HP_{ij}^{-1} = H$. There are N(N-1)/2 such transpositions that satisfy $P_{ij} = P_{ji} = P_{ij}^{-1}$. Since $P_{ij}^2 = \hat{E}$ (the identity operator) then the eigenvalues of every transposition operator are ± 1 . The invariance of H under transpositions can also be written in terms of vanishing commutators $[H, P_{ij}] = 0$. Since the transpositions do not commute, then we cannot obtain a complete set of eigenfunctions common to H and all P_{ij} . We can write a transposition as

$$P_{ij} = \begin{bmatrix} 1, 2, \dots, i, \dots, j, \dots N \\ 1, 2, \dots, j, \dots i, \dots N \end{bmatrix}$$

$$(1)$$

which means to substitute the electron variables \mathbf{r}_j , \mathbf{r}_i for \mathbf{r}_i , \mathbf{r}_j (it may also include spin variables when necessary)

The Hamiltonian H is also invariant under any permutation

$$P_{[i]} = \begin{bmatrix} 1, 2, \dots, N \\ i_1, i_2, \dots, i_N \end{bmatrix}$$

$$i_k \in \{1, 2, \dots, N\}$$
 (2)

which means to substitute \mathbf{r}_{i_1} , \mathbf{r}_{i_2} ,..., \mathbf{r}_{i_N} for \mathbf{r}_1 , \mathbf{r}_2 ,..., \mathbf{r}_N . There are N! such permutations of the variables of the N electrons that can be split into N!/2 even and N!/2 odd permutations. Any permutation can be written as a non-unique product of a finite number of transpositions [5]. However, given a permutation, the number of such factors is either even or odd and we commonly say that the permutation is even or odd, respectively. The set of all N! permutations of the N electrons form the symmetric group S_N . The invariance of the Hamiltonian

may be expressed either as $P_{[i]}HP_{[i]}^{-1}=H$ or $[H,P_{[i]}]=0$ for any of the N! permutations.

If ψ is an eigenfunction of H with eigenvalue E, then $P_{ij}H\psi=HP_{ij}\psi=EP_{ij}\psi$. Therefore, if ψ is non-degenerate then $P_{ij}\psi=\pm\psi$ for all i,j. In the case of a degenerate energy level both ψ and $P_{ij}\psi$ may be linearly independent eigenfunctions of H. In fact, since $[P_{ij},P_{kl}]\neq 0$ then the non-degenerate states are not, in general, eigenfunctions of all the permutation operators $P_{[i]}$. Despite of this fact it has been stated that $[H,P_{[i]}]=0$ implies that any eigenfunction of H is an eigenfunction of $P_{[i]}$ [1,6,7].

The Hamiltonians of some systems of identical particles are also invariant under coordinate inversion $\hat{i}f(\mathbf{x}) = f(-\mathbf{x})$ about the origin. Since $[H, \hat{i}] = 0$ and $[P_{ij}, \hat{i}] = 0$ then the eigenfunctions of H are either even or odd with respect to inversion: $\hat{i}\psi = \pm \psi$.

The results above apply to any system of N identical particles but we restrict ourselves to electrons because we are interested in the electronic structure of atoms (with the nucleus clamped at origin) and molecules (under the Born-Oppenheimer approximation). Since the Schrödinger equation for such systems cannot be solved exactly we resort to approximate methods. In order to obtain a suitable basis set for such calculations we commonly construct the required antisymmetric functions as Slater determinants [3]

$$|\chi_{i_1}\chi_{i_2}\dots\chi_{i_N}\rangle = \mathcal{A}\chi_{i_1}(1)\chi_{i_2}(2)\dots\chi_{i_N}(N)$$

$$= \frac{1}{\sqrt{N!}}\sum_{i=1}^{N!} (-1)^{p_{[i]}}P_{[i]}\chi_{i_1}(1)\chi_{i_2}(2)\dots\chi_{i_N}(N)$$
(3)

where $p_{[i]}$ reflects the parity (even or odd) of $P_{[i]}$ and χ_j is a spin-orbital given by the product of a space orbital factor φ_i and a spin one ω_k that equals either α ($m_s = 1/2$) or β ($m_s = -1/2$). The CI method is a Rayleigh-Ritz variational approach with the ansatz

$$\Phi = \sum_{i_1, i_2, \dots, i_N} C_{i_1, i_2, \dots, i_N} | \chi_{i_1} \chi_{i_2} \dots \chi_{i_N} \rangle$$
 (4)

commonly chosen to be an eigenfunction of the total spin operators S^2 and S_z when H is the non-relativistic (spin-free) Hamiltonian [3].

It is not possible to compare the approximate variational calculation based on the trial function (4) with an exact result because the Schrödinger equation for any atomic or molecular system with N > 1 cannot be solved exactly. For this reason in the following sections we consider two exactly solvable models with S_N symmetry.

3 Exactly-solvable three-particle model

The case N=2 is trivial because the only permutation operators are \hat{E} and P_{12} [2,5]. Therefore, any eigenfunction ψ of the non-relativistic Hamiltonian H satisfies $P_{12}\psi=\pm\psi$ and a symmetric spatial function is multiplied by an antisymmetric spin one (singlet state), whereas an antisymmetric spatial function is multiplied by a symmetric spin one (triplet) in order to obtain an antisymmetric total wavefunction Φ . Obviously, in this particular case we can easily omit the spin part in the construction of an approximate wavefunction. Therefore, the first non-trivial case is N=3.

The symmetric group S_3 is isomorphic to C_{3v} (and also to D_3) [8]; its character table being

$$\begin{array}{c|cccc} C_{3v} & \hat{E} & 2C_3 & 3\sigma_v \\ \hline A_1 & 1 & 1 & 1 \\ A_2 & 1 & 1 & -1 \\ E & 2 & -1 & 0 \\ \hline \end{array}$$

There is a one-to-one correspondence between the permutation operators and the C_{3v} ones given by

$$\hat{E} = \begin{bmatrix} 123 \\ 123 \end{bmatrix}, C_3 = \begin{bmatrix} 123 \\ 312 \end{bmatrix}, C_3^2 = \begin{bmatrix} 123 \\ 231 \end{bmatrix}
\sigma_{v_1} = \begin{bmatrix} 123 \\ 132 \end{bmatrix}, \sigma_{v_2} = \begin{bmatrix} 123 \\ 321 \end{bmatrix}, \sigma_{v_3} = \begin{bmatrix} 123 \\ 213 \end{bmatrix}$$

The well known projection operators

$$\mathcal{P}_{A_1} = \frac{1}{6} \left(\hat{E} + C_3 + C_3^2 + \sigma_{v_1} + \sigma_{v_2} + \sigma_{v_3} \right)$$

$$\mathcal{P}_{A_2} = \frac{1}{6} \left(\hat{E} + C_3 + C_3^2 - \sigma_{v_1} - \sigma_{v_2} - \sigma_{v_3} \right)$$

$$\mathcal{P}_E = \frac{1}{3} \left(2\hat{E} - C_3 - C_3^2 \right)$$

will be most useful for present analysis.

One can easily verify that the Hamiltonian

$$H = -\frac{1}{2} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} \right) + \frac{1}{2} \left(x_1^2 + x_2^2 + x_3^2 \right) + \xi \left(x_1 x_2 + x_1 x_3 + x_2 x_3 \right), \tag{5}$$

exhibits S_3 permutation symmetry and is parity invariant. It describes a system of three identical particles in a one-dimensional space that interact with a different one clamped at origin by means of the terms $x_j^2/2$ and between them by means of the terms $\xi x_i x_j$. It resembles, for example, the Lithium atom with the nucleus clamped at origin. One may reasonably argue that this one-dimensional toy model is unsuitable for the study of atomic systems but the point is that here we are merely interested in the permutation symmetry of the Hamiltonian operator. The great advantage of this simple model is that the Schrödinger equation is separable and exactly solvable. It is a simplified version of the oscillator models widely used by Moshinsky [4].

By means of the change of variables [2]

$$y_1 = \frac{\sqrt{2}x_2}{2} - \frac{\sqrt{2}x_3}{2}, \ y_2 = \frac{\sqrt{6}(2x_1 - x_2 - x_3)}{6}, \ y_3 = \frac{\sqrt{3}(x_1 + x_2 + x_3)}{3}, \ (6)$$

the Hamiltonian becomes

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

$$k = 1 - \xi, \ k' = 1 + 2\xi$$
(7)

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

$$\psi_{n_1 n_2 n_3}(x_1, x_2, x_3) = \phi_{n_1}(k, y_1)\phi_{n_2}(k, y_2)\phi_{n_3}(k', y_3)$$

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

$$n_1, n_2, n_3 = 0, 1, 2, \dots$$
(8)

where $\phi(k,q)$ is a normalized eigenfunction of the dimensionless Hamiltonian H_{HO} for the harmonic oscillator

$$H_{HO}\phi_n(k,q) = \sqrt{k} \left(n + \frac{1}{2} \right) \phi_n(k,q), \ n = 0, 1, \dots$$

$$H_{HO} = -\frac{1}{2} \frac{d^2}{dq^2} + \frac{k}{2} q^2$$
(9)

Since the symmetric group S_3 is isomorphic to C_{3v} we can label the irreps as A_1 , A_2 (both one-dimensional) and E (two-dimensional). If we added the inversion, then the suitable group would be D_{3h} (among others) with irreps A'_1 , A'_2 , E', A''_1 , A''_2 and E'', but we will restrict ourselves to the permutation symmetry. The Hamiltonian (5) exhibits also dynamical symmetry because it commutes with a set of five operators that depend on the coordinates and conjugate momenta. Consequently, the degeneracy of the energy levels given by n_1+n_2+1 is considerably greater than the one predicted even by D_{3h} . However, for present purposes it will suffice to consider just C_{3v} because we are interested only in the permutation symmetry. Note that the Hamiltonian operator for Lithium (under the clamped-nucleus approximation) commutes with the total angular momentum of the electrons L^2 and L_z ; therefore, the symmetric group S_3 will be insufficient in this realistic case too. Since the dynamical symmetry is model-dependent we will omit it from now on.

The variables y_1 and y_2 are basis for the irrep E while y_3 is basis for A_1 . For this reason all the states ψ_{00j} are basis for A_1 and the symmetry of the states of the non-relativistic Hamiltonian is completely determined by the quantum numbers n_1 and n_2 . For example, ψ_{10j} and ψ_{01j} are basis for E and the three degenerate functions with $n_1 + n_2 = 2$ are basis for both A_1 and E. The state ψ_{11j} is basis for E and by means of the projection operators we easily verify that the linear combinations $\psi_{20j} + \psi_{02j}$ and $\psi_{20j} - \psi_{02j}$ are basis for A_1 and E, respectively. We can carry out this analysis for every energy level; for example the four states with $n_1 + n_2 = 3$ are basis for A_1 , A_2 and A_3 . A straightforward calculation shows that $3\psi_{21j} - \psi_{03j}$, $\psi_{30j} - 3\psi_{12j}$ and $(\psi_{30j} + \psi_{12j}, \psi_{21j} + \psi_{03j})$ are basis for A_1 , A_2 and E, respectively. In this case only the basis functions

for the irreps A_1 and A_2 are eigenfunctions of all the permutation operators.

Let us now turn to the construction of antisymmetric spatial-spin functions. Since $\mathcal{P}_{A_2} = \sqrt{6}\mathcal{A}$ we will resort to this projection operator for the construction of antisymmetric functions. In the case of three electrons we expect one quadruplet and two doublets. In order to determine which non-relativistic functions will appear in a standard CI calculation we choose an arbitrary function $f(x_1, x_2, x_3)$ and construct antisymmetric functions according to the following expression

$$\mathcal{P}_{A_2}\omega_i(x_1)\omega_i(x_2)\omega_k(x_3)\mathcal{P}_uf(x_1,x_2,x_3) \tag{10}$$

where $u = A_1, A_2, E$. The procedure is quite simple: on inserting a product of three monoelectronic spin states the result may be zero or a valid Slater determinant. This straightforward calculation shows that the non-relativistic states that are basis for A_1 are not allowed by the principles of quantum mechanics. In other words, the non-degenerate energy levels E_{00j} will not appear in a CI calculation. The states that are basis for A_2 appear in the quadruplet, and those belonging to E in the doublets. It is worth noting that the conclusions based only on the permutation of the electron variables are model independent and therefore apply to more realistic models. For example, in the case of Lithium we expect approximate antisymmetric spatial-spin functions with spatial parts that are basis for the irreps A_2 (S = 3/2) and E (S = 1/2). In other words, we would obtain meaningful results with spin-free basis-set functions belonging to the symmetry species just mentioned. Also notice that equation (10) can be easily generalized to any number of electrons for which we only need the projection operators for the corresponding symmetric group.

It is not difficult to take into account that the Hamiltonian is also parity-invariant. We simply apply equation (10) with the projection operators \mathcal{P}_u for the symmetry point group D_{3h} ($u = A'_1, A'_2, E', A''_1, A''_2, E''$). The result is that A'_1 and A''_1 do not appear in the Slater determinants, A'_2 and A''_2 appear in the quadruplet, E' and E'' appear in the doublets. This result agrees with the analysis of the permutation symmetry of the hydrogen atoms in H_3^+ carried out,

for example, by Bunker and Jensen [10] and is called missing levels.

4 Exactly-solvable four-particle model

The symmetric group S_4 is isomorphic to O and T_d and we will choose the former point-group symmetry here. In this case we apply a somewhat different strategy. First, we derive the 24 matrices that produce all the permutations of the elements of a four-dimensional column vector \mathbf{x} . Second, we collect the matrices into their respective group classes and determine the order (also called period length) of each of them [8]. In this way we derive a one-to-one correspondence between the matrix classes and those appearing in the character table of the group O. Third, with each matrix \mathbf{M}_i we build the corresponding operator \hat{M}_i by means of the well known expression $\hat{M}_i f(\mathbf{x}) = f(\mathbf{M}_i^{-1}\mathbf{x})$. In this case we will show neither the character table nor the projection operators that can be easily constructed by means of well known expressions [8]. We will just discuss the results.

As an illustrative example we resort to the oscillator model

$$H = -\frac{1}{2} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} + \frac{\partial^2}{\partial x_4^2} \right) + \frac{1}{2} \left(x_1^2 + x_2^2 + x_3^2 + x_4^2 \right)$$

$$+ \xi \left(x_1 x_2 + x_1 x_3 + x_1 x_4 + x_2 x_3 + x_2 x_4 + x_3 x_4 \right)$$
(11)

that exhibits the appropriate symmetry. By means of the change of variables

$$y_{1} = \frac{1}{\sqrt{2}} (x_{1} - x_{4}), y_{2} = \frac{1}{\sqrt{2}} (x_{2} - x_{3}), y_{3} = \frac{1}{2} (x_{1} - x_{2} - x_{3} + x_{4}),$$

$$y_{4} = \frac{1}{2} (x_{1} + x_{2} + x_{3} + x_{4})$$
(12)

the resulting Hamiltonian is separable an exactly solvable

$$H = -\frac{1}{2} \left(\frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial y_3^2} + \frac{\partial^2}{\partial y_4^2} \right) + \frac{1-\xi}{2} \left(y_1^2 + y_2^2 + y_3^2 \right) + \frac{1+3\xi}{2} y_4^2$$
(13)

It exhibits bound states when $-1/3 < \xi < 1$ and its eigenfunctions and eigenvalues are given by

$$\psi_{n_1 n_2 n_3 n_4}(x_1, x_2, x_3, x_4) = \phi_{n_1}(k, y_1)\phi_{n_2}(k, y_2)\phi_{n_3}(k, y_3)\phi_{n_4}(k', y_4)$$

$$k = 1 - \xi, \ k' = 1 + 3\xi$$

$$E_{n_1 n_2 n_3 n_4} = \sqrt{1 - \xi} \left(n_1 + n_2 + n_3 + \frac{3}{2} \right) + \sqrt{1 + 3\xi} \left(n_4 + \frac{1}{2} \right)$$
 (14)

The degeneracy of the states of this oscillator is considerably greater than the one for the preceding example: $(n_1 + n_2 + n_3 + 1)(n_1 + n_2 + n_3 + 2)/2$.

The variables y_1 , y_2 , y_3 are basis for the irrep T_2 and y_4 is basis for A_1 . For this reason all the states of the form ψ_{000j} are basis for A_1 and the symmetry of the non-relativistic states is determined by the quantum numbers n_1 , n_2 and n_3 . For each value of n_4 the three degenerate states with $n_1 + n_2 + n_3 = 1$ are basis for T_2 . The six degenerate states with $n_1 + n_2 + n_3 = 2$ are basis for A_1 , E and E0. The ten degenerate states with E1 and E2 appear in a much higher energy level with E3. The basis functions for the irrep E4 appear in a much higher energy level with E4 and E5. As in the preceding example only the basis functions for the irreps E4 and E5 are eigenfunctions of all the permutation operators.

In order to determine which non-relativistic spatial functions contribute to the antisymmetric spatial-spin ones we proceed as in equation (10) adding an additional electron to that expression and choosing the projection operators for the symmetry point-group O. In the case of four electrons we expect one quintuplet, three triplets and two singlets. Our results show that the spatial functions that are basis for A_1 and T_2 are not allowed by the antisymmetry principle. The basis functions for A_2 , T_1 and E are responsible for the quintuplets, triplets and singlets, respectively. This conclusion is not model dependent because it is based entirely on the symmetry of the problem and applies, for example, to Beryllium under the clamped-nucleus approximation.

5 Further comments and conclusions

Throughout this paper we have analyzed the connection between the antisymmetric spatial-spin functions given in terms of Slater determinants and the eigenfunctions of the non-relativistic Hamiltonian that are basis for the irreps of the symmetric group S_N . We restricted ourselves to the particular cases of N=3

and N=4 electrons because they can be analyzed by means of the character tables of the point groups C_{3v} and O, respectively, that are well known for most chemists and physical chemists. The exactly solvable models chosen here are suitable for illustration but are not necessary for obtaining the main theoretical results. From the point of view of symmetry they are identical to the Lithium and Beryllium atoms and the particular forms of the Hamiltonians mimic those atoms in the clamped-nucleus approximation. However, the main conclusions about the symmetry of the spatial parts of the Slater determinants also applies to the case of finite nuclear mass. If we remove the motion of the center of mass and place the coordinate origin at the nucleus the resulting Hamiltonian exhibits the same symmetry S_N . The reason is that the coupling terms that appear in the kinetic-energy operator (the so called mass polarization terms) do not change the permutational symmetry of the Hamiltonians [9].

That the main theoretical results derived in this paper are not model dependent is clearly illustrated by the fact that present analysis of three 1/2-spin identical particles by means of the D_{3h} point group agrees with the results derived by Bunker and Jensen [10] for the hydrogen nuclei of the H_3^+ molecule.

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