

# Supplementary Material for the Manuscript ‘A nuclear spin and spatial symmetry-adapted full quantum method for light particles inside carbon nanotubes: clusters of $^3\text{He}$ , $^4\text{He}$ , and para- $\text{H}_2$ ’

María Pilar de Lara-Castells<sup>\*,†</sup> and Alexander O. Mitrushchenkov<sup>\*,‡</sup>

E-mail: Pilar.deLara.Castells@csic.es; Alexander.Mitrushchenkov@univ-eiffel.fr

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\*To whom correspondence should be addressed

<sup>†</sup>Instituto de Física Fundamental (AbinitSim Unit), CSIC, Serrano 123, 28006 Madrid, Spain

<sup>‡</sup>MSME, Univ Gustave Eiffel, UPEC, CNRS, F-77454, Marne-la-Vallée, France

## S1 Reduction of $S_N$ to $S_{N-1}$ symmetry for fermionic particles

As explained in the main text, the Hamiltonian expressed in internal coordinates does not explicitly include the symmetry group  $S_N$ . Yet, the solution must belong to the  $S_N$  representation as the original Hamiltonian features this symmetry. In order to identify the specific  $S_N$  representation, the symmetry of the solutions is tested *a posteriori*.

An acceptable solution for the case of spinless bosons must belong to the  $\{N\}$  Young diagram. By removing the coordinate of the particle labelled as  $N$ , this solution might only correspond to the  $\{N-1\}$  diagram of the  $S_{N-1}$  group as it must obviously be symmetric with respect to any permutation of first  $N-1$  PNs. However, the solution that transforms as the  $\{N-1\}$  representation of the  $S_{N-1}$  symmetry group may correspond not only to the  $\{N\}$  but also to the  $\{N-1, 1\}$  diagram of  $S_N$ . To verify that we have calculated a good  $\{N\}$  solution, a ‘symmetry factor  $Q$ ’ is evaluated as:

$$Q \equiv \langle \Psi(1 \leftrightarrow N) | \Psi \rangle.$$

Then, from general theory of the  $S_N$  group representations,<sup>1</sup> it can be shown that the factor  $Q$  for the solution corresponding to  $\{N\}$  ( $\{N-1, 1\}$ ) is equal to  $+1$  ( $-\frac{1}{N-1}$ ). Therefore, the factor  $Q$  can be used to select the correct solutions. We note that it involves a modification of the DVR basis grid, and thus may also serve as a numerical indicator of its quality itself.

A similar approach can be used for the fermionic case. The total wave function of  $N$  fermions with a total spin  $S$  and its projection  $M$  can be written as<sup>1</sup>

$$\Psi_i = \frac{1}{\sqrt{f}} \sum_{j=1}^f X(N, S, M; f) \Phi_{ji}^S$$

where the index  $i$  labels the solution, and the (normalized) spin functions  $X(N, S, M; f)$  transform according to the  $\{\frac{N}{2} + S, \frac{N}{2} - S\}$  representation of the  $S_N$  group,  $f$  being the dimension of this representation. For example, these can be branching diagram functions arranged to the last letter sequence. The (normalized) spatial wave functions  $\Phi_{ji}^S$  then transform according to a conjugate

representation. As the structure of this representation depends on  $S$ , these functions also depend on  $S$  as indicated by superscript, but are independent on  $M$ . The conjugate representation is obtained by transposing the Young tableau of the spin part, and including the permutation parity phase into the representation matrices.<sup>1</sup> Then, the (spin-free) Hamiltonian evaluated over the functions  $\Phi_{ji}^S$  becomes proportional to the unit matrix, with the diagonal value as the corresponding energy  $E_i$ .

For the Hamiltonian expressed in internal coordinates, we can only explicitly consider the  $S_{N-1}$  symmetry operation so that the  $S_N$  representation has to be reduced to the corresponding  $S_{N-1}$  ones. Different  $S_{N-1}$  representations may correspond to a given spatial conjugate representation of  $S_N$ , as the reduction is achieved by simple removal of the Young tableau cell containing the coordinate of the particle labelled as  $N$ . The Hamiltonian matrix over all corresponding functions will be the same (i.e., having the same energy value  $E_i$  on the diagonal). To identify to which  $S_N$  representation our  $S_{N-1}$  solutions belong, the matrix of  $Q$  factors must be evaluated. A general approach can be implemented using the above expressions but, for illustrative purposes, we next will consider the specific cases with  $N = 2, 3$ , and 4.

### **S1.1** $N = 2$

As described in the main text, the full  $S_2$  permutation symmetry is explicitly incorporated for the case with  $N = 2$ . For fermionic particles, it implies that, for symmetric spin wave-functions (triplet, the  $\{2\}$  representation of  $S_2$ ), the spatial part must be anti-symmetric while, for anti-symmetric spin-function (singlet,  $\{1, 1\}$  representation), the spatial part must be symmetric. For  $N = 2$ , it is thus not necessary to calculate the symmetry factors  $Q$ .

### **S1.2** $N = 3$

For the case of  $N = 3$  fermionic particles, the spin  $S$  can adopt the values of  $3/2$  and  $1/2$ . For  $S = 3/2$ , the spin part transforms as the  $\{3\}$  representation of the  $S_3$  group (i.e., it is fully symmetric). It follows that the spatial part transforms as  $\{1, 1, 1\}$  (i.e., it is fully anti-symmetric). Clearly, by removing the coordinate of the 3rd particle, the corresponding representation of  $S_2$  is  $\{1, 1\}$ . This

representation, apart from  $\{1, 1, 1\}$  of  $S_3$ , can also be obtained by reducing the  $\{2, 1\}$  representation of the  $S_3$  group. The representation  $\{1, 1\}$  is one-dimensional and, by calculating the  $Q$  factor, it is easy to distinguish between the two solutions. The solution corresponding to  $\{1, 1, 1\}$  and  $\{2, 1\}$  of the  $S_3$  group have  $Q = -1$  and  $Q = 1/2$ , respectively. In order to obtain the correct  $S = 3/2$  spin solution, the  $\{1, 1\}$  symmetry of the  $S_2$  group has to be imposed, as followed by a test with the  $Q$  factor evaluation. Once again, the  $Q$  factor will serve as the test for the grid quality.

For  $S = 1/2$ , the spin part transforms according to  $\{2, 1\}$  representation. Therefore, the spatial part transforms according to  $\{2, 1\}$  (conjugate) as well. Reducing to  $S_2$ , it can be obtained from either  $\{1, 1\}$  or  $\{2\}$  representations. We note that the  $\{2, 1\}$  representation of  $S_3$  is two-dimensional. Both corresponding  $\{1, 1\}$  and  $\{2\}$  representations of  $S_2$  themselves are non-degenerate. It is easy to obtain the  $Q$  factors corresponding to the  $\{2, 1\}$  solution: it is  $Q = 1/2$  for  $\{1, 1\}$  and  $Q = -1/2$  for  $\{2\}$ . The energies of these solution belonging to different  $S_2$  representations, should be degenerate. This degeneracy, together with  $Q$  values, again constitutes a good test of the quality of the grid. For  $\{2\}$  representation of  $S_2$  we may also have the  $Q$  factor of  $+1$  that corresponds to “spurious” (bosonic-like) solution as discussed above for bosons.

### **S1.3** $N = 4$

For the case of  $N = 4$  fermionic particles, the spin  $S$  can adopt the values of 0, 1 and 2. For  $S = 2$ , the spatial part transforms as a fully anti-symmetric function (i.e., as the  $\{1, 1, 1, 1\}$  representation of the  $S_4$  group). This is a one-component function obtained from the  $\{1, 1, 1\}$  representation of the  $S_3$  group, which is also non-degenerate. The  $Q$  factor must be  $-1$  for the  $\{1, 1, 1\}$  solution with  $S = 2$ . This result is rather obvious and similar to the case of  $S = 3/2$  for  $N = 3$ .

For  $S = 1$ , the spin function transforms as the  $\{3, 1\}$  representation. Accordingly, the spatial contribution must transform as the conjugate  $\{2, 1, 1\}$  of the  $S_4$  symmetry group. Both representations are three-dimensional so that the full (spin and spatial) wave-function contains three terms. For the spatial wave-function, one term arises from the  $\{1, 1, 1\}$  representation of the  $S_3$  group which is non-degenerate, with  $Q = 1/3$ . To illustrate the previous general considerations, let us consider

this case in more detail. The three Young tableau corresponding to the  $\{2, 1, 1\}$  diagram, as well as the conjugate representation, are written as follows:

1	4
2	
3	

1	3
2	
4	

1	2
3	
4	

After removing the coordinate of the 4-th particle from the symmetry operations, it is clear that the first function belongs to the  $\{1, 1, 1\}$  representation, while the other two components form the basis of the two-dimensional  $\{2, 1\}$  representation. If the representation is not one-dimensional, the numerical solver can produce arbitrary linear combinations of degenerate solutions. Instead of a single  $Q$  factor, we have to calculate the sum over the degenerate components (i.e., the trace of the  $Q$  matrix over the degenerate states). Once again, from general representation theory, it follows that the trace of  $Q$  factors over  $\{2, 1\}$  representation (last two tableau's above) should be  $Q = -4/3$  for the solution corresponding to  $S = 1$ . We stress again that the energies of these two  $\{2, 1\}$   $S_3$  symmetry solutions should be equal and degenerate with the corresponding  $\{1, 1, 1\}$  solution (having  $Q = 1/3$ ). Once more, the occurrence of this degeneracy together with the determination of accurate  $Q$  values (i.e., differing very little from the ‘nominal values’) are good tests for the grid quality.

Finally, for  $S = 0$ , both the spin and spatial WF contributions transform as the  $\{2, 2\}$  representation. This is a two-dimensional representation. Its two spatial components come from the  $\{2, 1\}$  symmetry of the  $S_3$  group, with a trace of the  $Q$  factor equal to zero.

## S2 Details of the *ab initio*-derived pairwise potential model

The details of the *ab initio*-derived potential model used in this work for the He–SWCNT(11,4) interaction have already been provided in Ref. 2. As mentioned in the main text, our model uses different analytical forms for the dispersionless and dispersion energy contributions. For convenience, we outline here the most important details.

The interaction between a given pseudo-nucleus (referred to as PN) and the SWCNT tube accounts for the typical exponential growth of the dominant dispersionless contribution, the exchange-repulsion, but also including a Gaussian-type ‘cushion’ to characterize weakly attractive tails stemming from other dispersionless terms as follows

$$E_{\text{int}}^{\text{disp-less}}(\{\mathbf{R}_{\text{A-C}}\}) = \sum_{\text{C}} [1 + \gamma_{\text{R}}(1 - \frac{6}{5} \cos^2 \theta_{\text{C}})] \\ \times A e^{(-\alpha : R_{\text{A-C}} - \beta R_{\text{A-C}}^2)}, R_{\text{A-C}} < R_{\text{c}}.$$

$R_{\text{c}}$  is a cut-off distance,  $R_{\text{A-C}}$  stands for the distance between the adsorbate and one carbon atom of the SWCNT nanotube, and  $\theta_{\text{C}}$  is the angle between the radial vector going from the nanotube center to one carbon atom and the vector  $\mathbf{R}_{\text{A-C}}$  pointing from the adsorbate to the same C atom. The dimensionless factor  $\gamma_{\text{A}}$  in the first term accounts for the anisotropy of the C–C bonds. The sum in the second term runs over all carbon atoms of the SWCNT(11,4) nanotube. Aimed to model the dispersion contribution, we apply the typical  $\text{C}_6/\text{C}_8$  expansion with the damping functions of Tang and Toennies  $f_n$  ( $n = 6, 8$ )<sup>3</sup>

$$E_{\text{int}}^{\text{disp}}(\{\mathbf{R}_{\text{A-C}}\}) = - \sum_{\text{C}} [1 + \gamma_{\text{A}}(1 - \frac{3}{2} \cos^2 \theta_{\text{C}})] \\ \times \sum_{n=6,8} \frac{\sqrt{C_{\text{n}}^{\text{A}} C_{\text{n}}^{\text{C}}}}{R_{\text{A-C}}^n} f_n \left( \sqrt{\beta_{\text{A}} \beta_{\text{C}}} R_{\text{AC}} \right),$$

where  $\gamma_{\text{R}}$  is also a dimensionless anisotropy parameter. The explicit form of the damping functions is

$$f_i(x) = 1 - \sum_{j=0}^i \frac{x^j}{j!} \exp(-x)$$

The fitting parameters have been provided in the Supporting Information of Ref. 4. These model parameters were derived by fitting the dispersionless and dispersion contributions, as calculated using the Density Functional Theory (DFT)-Based Symmetry Adapted Perturbation Theory<sup>5-7</sup> approach.

We have used the same *ab initio*-derived potential model for the  $\text{H}_2$ –SWCNT(11,4) interaction,

with the details having been provided in Ref. 8 (see section S2 of the corresponding Supporting Information<sup>8</sup>). In order to employ these potentials within the DVR approach, they were fit to the polynomials of the order six of  $\rho$ :

$$V_1(\rho) = \sum_{l=0}^{l_{max}} p_l \rho^l \quad (\text{S1})$$

with  $l_{max} = 6$ .

The parameters of the fit are provided in Table S1. The values bearing machine precision are available from the authors upon request.

Table S1: Parameters of the potential fit  $p_l$  for the PN-SWCNT(11,4) interaction, see Eq.(S1).  $p_l$  are in  $\text{cm}^{-1}$  and  $\rho$  in  $a_0$ .

$l$	0	1	2	3	4	5	6
D <sub>2</sub> , H <sub>2</sub>	-394.920	-86.761	-4.658	0.478	0.270	$0.497 \times 10^{-1}$	$-0.258 \times 10^{-2}$
<sup>4</sup> He, <sup>3</sup> He	-127.510	-14.750	-17.277	6.438	-1.014	$0.936 \times 10^{-1}$	$-0.148 \times 10^{-2}$

### **S3 One-dimensional cuts of the one-particle densities for the ground states of the PN<sub>N</sub>-SWCNT(11,4) complexes (PN=<sup>3</sup>He, <sup>4</sup>He, para-H<sub>2</sub>)**

To complete the presentation of 2D density plots in the main text, Figures S1-S3 shows 1D density plots for the ground states of the PN<sub>N</sub>-SWCNT(11,4) complexes (PN=<sup>3</sup>He, <sup>4</sup>He, para-H<sub>2</sub>), including comparison with the ortho-D<sub>2</sub> counterpart. The 1D density is defined as the square of the corresponding WF integrated over all but one coordinate. For completeness, we provide also the density in the coordinates  $\rho$ .

Figure S1: Plot of 1D densities for the ground state of  $\text{PN}_2 \subset \text{SWCNT}(11,4)$  complexes. Left to right:  $\text{PN}=\text{}^3\text{He}$ ,  $\text{}^4\text{He}$ , para- $\text{H}_2$ , ortho- $\text{D}_2$ . (a) coordinate  $\rho$ ; (b) coordinate  $t$ ; (c) coordinate  $\chi$ .

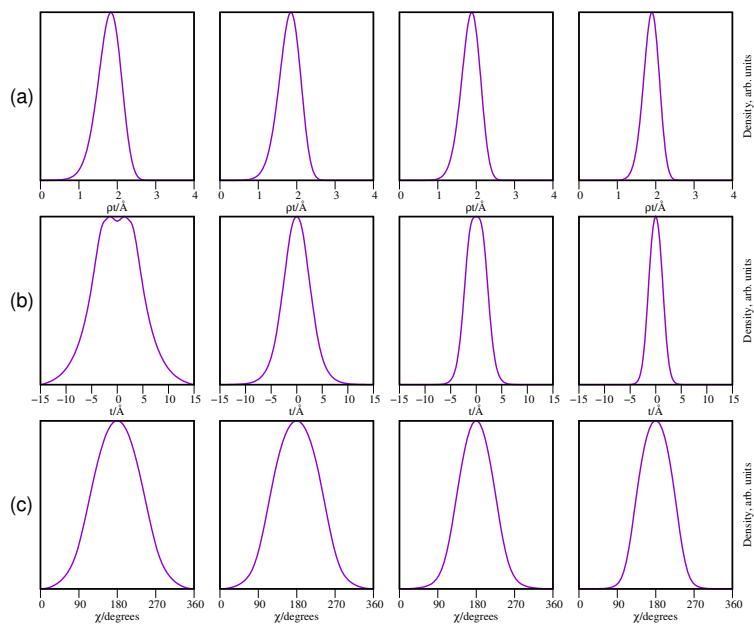


Figure S2: Plot of 1D densities for the ground state of  $\text{PN}_3 \subset \text{SWCNT}(11,4)$  complexes. Left to right:  $\text{PN}=\text{}^3\text{He}$ ,  $\text{}^4\text{He}$ , para- $\text{H}_2$ . (a) coordinate  $\rho$ ; (b) coordinate  $t$ ; (c) coordinate  $\chi$ .

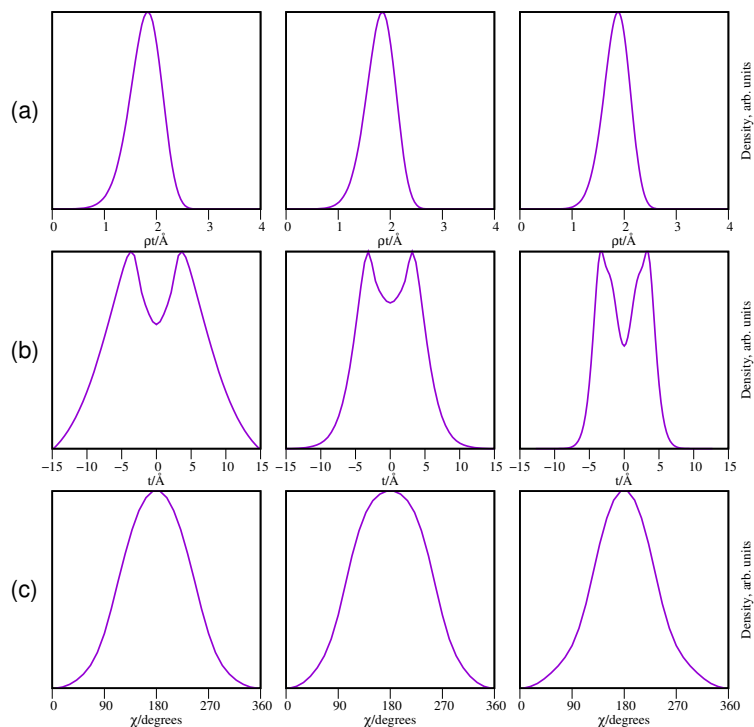
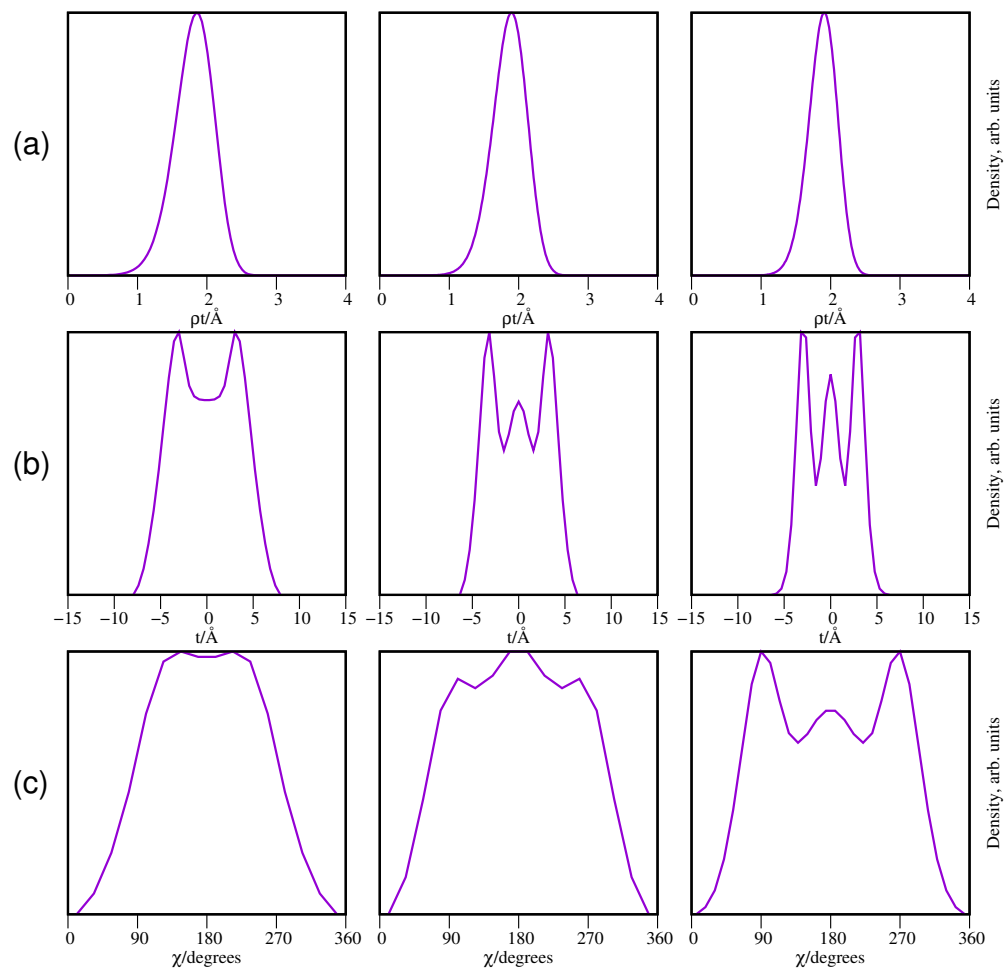




Figure S3: Plot of 1D densities for the ground state of  $\text{PN}_4 \subset \text{SWCNT}(11,4)$  complexes. Left to right:  $\text{PN}=\text{}^4\text{He}$ , para- $\text{H}_2$ , ortho- $\text{D}_2$ . (a) coordinate  $\rho$ ; (b) coordinate  $t$ ; (c) coordinate  $\chi$ .



## References

- (1) Pauncz, R. *The Symmetric Group in Quantum Chemistry*; Mathematical Chemistry; Taylor & Francis, 1995.
- (2) Hauser, A. W.; Mitrushchenkov, A. O.; de Lara-Castells, M. P. Quantum Nuclear Motion of Helium and Molecular Nitrogen Clusters in Carbon Nanotubes. *J. Phys. Chem. C* **2017**, *121*, 3807–3821.
- (3) Tang, K. T.; Toennies, J. P. An Improved Simple-Model for the van der Waals Potential Based on Universal Damping Functions for the Dispersion Coefficients. *J. Chem. Phys.* **1984**, *80*, 3726–3741.
- (4) de Lara-Castells, M. P.; Hauser, A. W.; Mitrushchenkov, A. O.; Fernández-Perea, R. Quantum Confinement of Molecular Deuterium Clusters in Carbon Nanotubes: *Ab Initio* Evidence for Hexagonal Close Packing. *Phys. Chem. Chem. Phys.* **2017**, *19*, 28621–28629.
- (5) Misquitta, A. J.; Podeszwa, R.; Jeziorski, B.; Szalewicz, K. Intermolecular Potentials Based on Symmetry-Adapted Perturbation Theory with Dispersion Energies from Time-Dependent Density-Functional Calculations. *J. Chem. Phys.* **2005**, *123*, 214103.
- (6) Heßelmann, A.; Jansen, G.; Schütz, M. Density-Functional-Theory Symmetry-Adapted Intermolecular Perturbation Theory with Density Fitting: A New Efficient Method to Study Intermolecular Interaction Energies. *J. Chem. Phys.* **2005**, *122*, 014103.
- (7) Heßelmann, A.; Jansen, G. Intermolecular Dispersion Energies from Time-Dependent Density Functional Theory. *Chem. Phys. Lett.* **2003**, *367*, 778–784.
- (8) de Lara-Castells, M.; Mitrushchenkov, A. O. From Molecular Aggregation to a One-Dimensional Quantum Crystal of Deuterium Inside a Carbon Nanotube of 1 nm Diameter. *J. Phys. Chem. Lett.* **2020**, *11*, 5081–5086.