A full-configuration interaction “nuclear orbital” method to study doped $^3\text{He}_N$ clusters ($N \leq 4$)

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An efficient full configuration interaction (FCI) treatment, based on the Jacobi-Davidson algorithm, is developed in order to study small doped $^3\text{He}_N$ clusters. The state of each He atom in a given cluster is described by a set of wave-functions which by extension of the quantum-chemistry notation are called here “nuclear orbitals”. The FCI treatment is applied to the calculation of binding energies and helium natural orbitals of $^3\text{He}_N \cdots \text{Br}_2(X)$ complexes. In agreement with our previous calculations using a Hartree-Fock approach [Phys. Rev. Lett. **93**, 053401 (2004)], in which the He–He interaction is modified at small distances to account for short-range correlation effects, the lowest-energy states of each multiplet are found to be very close in energy. The natural orbital analysis, in turn, indicates the adequacy of the “nuclear orbital” approach in these systems. © 2006 American Institute of Physics. [DOI: [10.1063/1.2403846](https://doi.org/10.1063/1.2403846)]

Spectroscopic experiments on molecules embedded in helium clusters have revealed a number of unusual features deriving from the unique quantum behavior of this environment.¹ The marked difference observed by Grebenev *et al.*^{2,3} in the infrared spectra of carbonyl sulfide (OCS) surrounded by helium atoms which depends on the isotope considered, ^3He or ^4He , is one of the experimentally most well-documented evidence of this feature. For ^4He , sharp profiles resembling those of isolated OCS are observed, while for ^3He the spectrum merges into a broadband, as occurs for heavy molecules immersed in a normal liquid. After the addition of about sixty ^4He atoms the structured spectrum is recovered, a feature which was attributed to the onset of superfluidity in a microscopic system, similar to what happens in liquid ^4He .

Powerful computational tools and theoretical approaches to describe ground-state properties of both pure and doped ^4He clusters⁴ have been provided by zero temperature diffusion Monte Carlo (DMC)⁵ and finite temperature Feynman’s path-integral Monte Carlo methods.⁶ Further, the reptation quantum Monte Carlo approach,⁷ or the projection imaginary time spectral evolution implementation of the DMC method,⁸ also can provide the low-lying excited states, the first experimental conformation for the excited energy levels of neutral⁴ clusters being provided by Brühl *et al.*⁹ In the case of ^3He clusters the status of these methodologies is far behind those of their ^4He counterparts. The extension of DMC methods to fermionic clusters presents an obvious difficulty in the nodal structure of the wavefunction. An upper bound to the ground-state energy is obtained by the fixed-node (FN) approximation,¹⁰ but its quality largely depends on the trial wave function. Using the released-node tech-

nique, an estimation of the bias introduced by the FN approximation can be obtained.¹¹

The field of *ab initio* electronic structure theory is the framework in which, perhaps, the many-body problem has been studied at the deepest level. So, quantum-chemistry-type approaches where the dopant molecule and the He atoms play the role of the nuclei and electrons, respectively, have recently emerged. This approach was first proposed by Jungwirth and Krylov¹² and applied to the lowest-energy triplet state of $^3\text{He}_2\text{--SF}_6$. Unlike other alternative approaches, such as those based on density functional theory [see, e.g., Ref. 13], the appealing advantage of wave function-based quantum chemistry treatments is that they allow for spectral simulations of the dopant molecule and other possible observables. Hartree/Hartree-Fock approaches recently have been developed and applied to the simulation of vib-rotational Raman spectra of bosonic, fermionic, and mixed $\text{Br}_2(X)\text{--He}_N$ clusters^{14,15} as well as infrared spectra of the ICl molecule embedded in a bath of $^4\text{He}_N$ clusters.¹⁶ The quality of the Hartree approach¹⁷ for boson environments, regarding energetics as well as structural properties, was assessed through DMC calculations.¹⁸ The simulations chiefly stress the key role of nuclear spin statistical quantum effects in determining the different spectra that were observed experimentally. In the case of doped ^3He clusters, the high degeneracy found for different spin-multiplets causes the appearance of many overlapping lines. This produces a congestion of the spectrum, which then consists of an broad unstructured band. As ^4He atoms are added to a fermionic cluster, the degeneracy is gradually reduced and the spectral profile recovers an essentially bosonic well-defined structure.

The next step toward more rigorous approaches is to include explicitly the He–He correlation and the excited states. In this work, we implement an efficient full-configuration interaction (FCI) approach, based on the

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Jacobi-Davidson (JD) algorithm.¹⁹ In order to verify the previous Hartree-Fock results,¹⁴ the approach is applied to the calculation of the binding energies and helium wave functions of ${}^3\text{He}_N\text{-Br}_2(X)$, $N \leq 4$, not only for their ground but also for the low-lying excited states with all possible spin multiplicities.

Keeping the diatomic bond length r fixed, choosing a body-fixed frame in which the Z axis is parallel to the diatomic bond (i.e., the diatom does not rotate), and using satellite coordinates $\{\mathbf{R}_k\}$, which are the vectors going from the center of mass of the diatomic molecule to the different He atoms, one can write the Hamiltonian associated with the motion of the N helium atoms as

$$H^{(N)} = \sum_{k=1}^N h_k(\mathbf{R}_k, r) + \sum_{k < l} V_{kl}(|\mathbf{R}_k - \mathbf{R}_l|) - \frac{\hbar^2}{m_{AB}} \sum_{k < l} \nabla_k \cdot \nabla_l, \quad (1)$$

consisting of N He-AB triatomic Hamiltonians plus all the He-He interactions that includes potential terms and also kinetic He-He couplings.²⁰ The potential energy of the system is thus represented as a sum of N He-AB triatomic plus He-He pair interactions. The validity of this approach has been evaluated through *ab initio* calculations on $\text{He}_2\text{-Br}_2$ and $\text{He}_2\text{-ICl}$ systems.^{21,22}

In Eq. (1) each triatomic Hamiltonian has the form

$$h_k(\mathbf{R}_k, r) = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R_k^2} + \frac{\mathbf{I}_k^2}{2\mu R_k^2} + W(R_k, r, \theta_k), \quad (2)$$

where μ is the reduced mass of the He-AB sub-system, $\mathbf{I}_k$ is the angular momentum associated with $\mathbf{R}_k$, and W represents the atom-diatom intermolecular potential that depends on the pair of (R_k, r) distances and on the polar angle θ_k . So within an adiabatic approach we have to solve the Schrödinger equation

$$[H^{(N)} - E_{\Gamma, S}^{(N)}(r)]\Phi_{\Gamma, S}^{(N)}(\{\mathbf{R}_k\}; r) = 0 \quad (3)$$

for different fixed values of r . In Eq. (3), each r -dependent eigenvalue and the corresponding eigenfunction are labeled according to the irreducible representation of the symmetry group ($C_{\infty v}$ or $D_{\infty h}$) of the diatomic (heteronuclear or homonuclear) molecule Γ , and the total spin angular momentum S .

The spatial single-particle wavefunctions entering the Slater determinants were expanded using a finite basis set composed of products of radial and angular functions,

$$\chi^{(n\ell m)}(\mathbf{R}; r) = G_n(R; r) Y_{\ell m}(\theta, \phi), \quad (4)$$

where $Y_{\ell m}(\theta, \phi)$ are spherical harmonics. The radial basis functions $G_n(R; r)$ are obtained from the lowest energy solutions of the Schrödinger equation that correspond to the ${}^3\text{He-AB}$ triatomic subsystem with a fixed value of θ_n ,

$$\left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + W(R; r; \theta_n) - E_n(r) \right] g_n(R; r; \theta_n) = 0. \quad (5)$$

The calculations were performed for $n_{\max}$ different equidistant values of θ_n in the range $[0, \pi]$. The radial basis used in Eq. (4) is finally obtained from the radial functions $g_n(R; r; \theta_n)$ through Schmidt orthogonalization. Detailed ex-

pressions for the evaluation of the integral as well as the one-particle density are provided in Ref. 17. Through the expansion of the one- and two-body potential energy terms of Eq. (3) in Legendre polynomials, these expressions involve just two-dimensional radial integrals which are evaluated numerically.

The integral evaluation program was interfaced to an efficient full configuration interaction (FCI) code, which is a modified version of the dynamic CI program.²³ This full CI program is based on configuration state functions (CSF) and contains efficient hand-coded routines for a small number of fermions. Expressions for the coupling coefficients in the CSF basis can be found, e.g., in Ref. 24. The functions used to construct the CSFs are not the original “atomic” orbitals but rather their linear combinations. They correspond to molecular orbitals in quantum chemistry. Integral transformation to these orbitals is performed before the FCI run. The molecular orbitals were selected to provide better convergence of the iterative full CI procedure. In practice, we used the natural orbitals obtained from the preceding calculation of the ground state with $N-1$ particles.

Due to the large size of the FCI configuration space, it is only possible to use a so-called “direct-CI” iterative methods, where the matrix to diagonalize is never evaluated and stored but rather its action on a given trial vector is provided. In quantum-chemistry calculations the Davidson method²⁵ is nearly always used. Its advantage is that no additional matrix-vector operation is needed for a given iteration, and typically converges quickly (from 20 to 30 iterations) to chemical accuracy. The success of the Davidson algorithm, where the Hamiltonian is approximated by its diagonal for a Newton-Raphson correction, is based on the fact that typical quantum-chemistry Hamiltonians are diagonally dominant. In contrast we found that, in our case, due to the strong repulsion of both He-He and He-AB interactions at short distances, very large off-diagonal Hamiltonian elements appear. Even using natural orbitals for some CI state the corresponding Hamiltonian matrix contains very high positive values on the diagonal and similar off-diagonal terms that, in turn, are a few orders of magnitude larger than the final (negative) eigenvalues. In these conditions we have found that the standard Davidson algorithm has very poor convergence. Consequently, we have incorporated the Jacobi-Davidson (JD) modification¹⁹ of the original Davidson algorithm. In the JD method, one approximately solves the Newton-Raphson correction equation iteratively, similar to Davidson algorithm, for each Davidson macro iteration. In our program, we used the SYMMLQ solver²⁶ which we found to have superior convergence in our case, as compared to the MINRES²⁶ method.

We have applied our FCI approach to the calculation of the energies and helium wave functions of $({}^3\text{He})_N\text{-Br}_2$ clusters, $N \leq 4$, in their ground and low-lying excited states with all possible spin multiplicities. As in our previous works,^{14,15,17} the ${}^3\text{He-Br}_2$ PES was taken as a pairwise addition of Morse-type He-Br pair interactions and the He-He interaction was described by a model potential.²⁷ We used the same basis set as in Refs. 14 and 15: $l_{\max}=8$, $|m_{\max}|=3$, and $n_{\max}=4$ (i.e., 176 orbitals, which were classified with

FIG. 1. Energy ($N=4$, ${}^3\Sigma_g^-$ state) for Jacobi-Davidson (open squares) and Davidson (full squares) procedures as a function of the number of iterations. The converged, “exact”, energy is also shown.

respect to the irreducible representations of the D_{2h} point group—the highest symmetry group that we can be used in our CI program). The Br–Br bond length was fixed to its equilibrium value (2.281 Å).

In Fig. 1 we first compare the convergence of Davidson and JD methods applied to the calculation of the ground-state energy of the $({}^3\text{He})_4\text{--Br}_2$ complex. In that case, the dimension of the FCI space was about 15 million of CSFs. Each JD iterative solver used 40 internal JD iterations, thus one JD result is presented at each 40 Davidson iterations. Note the fast convergence of the JD procedure as compared to the standard Davidson one. After just 30 outer JD iterations (the 1200th iteration in Fig. 1), the energy has converged to within 10^{-4} cm^{-1} . At the 50th outer iteration, the energy has converged to the desired accuracy (10^{-10} cm^{-1}), and the norm of the residual vector [defined as $(E - \hat{H})\mathbf{C}$] is less than 10^{-3} . Thus, the total required Hamiltonian applications is about 2000. In contrast, after 1500 iterations of the Davidson procedure (see Fig. 1), the energy is still 3.9 cm^{-1} above the “exact” energy, the norm of the residual being very large (5.9 cm^{-1}). Also, in contrast to the JD procedure, the energy differences $E^{(i)} - E^{(i-1)}$ show a strong oscillatory behavior. At the 30 000th iteration, the energy (norm of residual) is still

0.05 (1.0 cm^{-1}) too high. In fact, it was not possible to converge the norm of residual to less than 10^{-2} cm^{-1} through the Davidson procedure.

The full-CI energies of the $({}^3\text{He})_N\text{--Br}_2$ clusters are displayed in Table I. The different states have been classified according to the number of fermions (N), the total spin (S), and the irreducible representations within the D_{2h} symmetry group. We first stress the high degree of degeneracy of the different lowest-energy spin states. For any number of particles, the energy differences among of the lowest states of each multiplet are less than 1 cm^{-1} . This is in agreement with our previous calculations using a Hartree-Fock approach, constructed by truncating the true He–He interaction at small distances to account for correlation effects. In fact, except in the Pauli suppressed triplet state of the $({}^3\text{He})_2\text{--Br}_2$ complex, Hartree-Fock energies using the bare He–He potential are unphysically too large [i.e., -9.880 cm^{-1} for the ground state of the $({}^3\text{He})_3\text{--Br}_2$ complex] and positive in many cases (i.e., the ground state for $N=2$). The introduction of the He–He correlation makes all complexes bound. Turning to the FCI energies in Table I, we note that for $N=4$ a very dense excitation spectrum appears. In particular, note the high-degeneracy (within less than 0.6 cm^{-1}) of the inversion-related (g/u) symmetry pairs. For instance, the energy splitting between the ground-state (${}^3\Sigma_g^-$) and the inversion-symmetry counterpart (the ${}^3\Sigma_u^-$ state) is less than 0.2 cm^{-1} . Also, at $N=4$, the rather linear behavior of the ground-state energies with N breaks. This is an indication that the first subshell may be made up of the lowest three orbitals.

In Table II we give a list of the occupation numbers, referred to as η , of the natural orbitals,²⁸ which are the eigenvalues of the first order density matrix. The first He populates the lowest-energy (-15.467 cm^{-1} , Table I) $1\sigma_g^+$ orbital. For $N=2$, the η values clearly reflect significant contributions of virtual excitations from the $1\sigma_g$ natural orbital to the $1\pi_u$ one. The ground-state wave function for $N=3$ is dominated (with a coefficient of 0.90) by the triplet configuration ($1\sigma_g$) ($1\pi_u$) ($1\pi_u$), although there is also significant configurational mixing with the $1\delta_g$ natural orbital, the η value being about 10% of the total population. For $N=4$, the population becomes effectively distributed over a larger number of natural orbitals (about 9), the filling of the $2\sigma_g^+$ one ($\eta \sim 0.8$) being particularly noteworthy. On the whole, the

TABLE I. Energies (in cm^{-1}) of $({}^3\text{He})_N\text{--Br}_2$ clusters using the Jacobi-Davidson based FCI treatment. The different states are classified according to the number of fermions (N), the total spin (S), and the symmetry within the D_{2h} point group (the corresponding $C_{\infty v}$ symmetry is indicated in parenthesis). Values in boldface correspond to the lowest energy states within a given (N , S) manifold.

N	S	A_g	B_{3u}/B_{2u}	B_{1g}	B_{1u}	B_{2g}/B_{3g}	A_u
1	1/2	-15.467 (${}^2\Sigma_g^+$)	-15.206(${}^2\Pi_u$)	-13.956(${}^2\Delta_g$)	-9.581(${}^2\Sigma_u^+$)	-9.027(${}^2\Pi_g$)	-7.970(${}^2\Delta_u$)
2	0	-30.706 (${}^2\Sigma_g^+$)	-29.487(${}^1\Pi_u$)	-29.902(${}^1\Sigma_g^-$)	-24.725(${}^1\Sigma_u^+$)	-24.586(${}^1\Pi_g$)	-24.114(${}^2\Sigma_u^-$)
	1	-29.036(${}^3\Sigma_g^+$)	-30.570 (${}^3\Pi_u$)	-30.066(${}^3\Sigma_g^-$)	-24.796(${}^3\Sigma_u^+$)	-24.571(${}^3\Pi_g$)	-24.004(${}^3\Sigma_u^-$)
3	1/2	-42.718(${}^2\Delta_g$)	-44.360 (${}^2\Pi_u$)	-42.718(${}^2\Delta_g$)	-39.228(${}^2\Sigma_u^+$)	-39.102(${}^2\Pi_g$)	-39.333(${}^2\Sigma_u^-$)
	3/2	-37.129(${}^4\Sigma_g^+$)	-37.948(${}^4\Pi_u$)	-45.196 (${}^4\Sigma_g^-$)	-38.715(${}^4\Sigma_u^+$)	-39.250(${}^4\Pi_g$)	-39.246(${}^4\Sigma_u^-$)
4	0	-50.451(${}^1\Sigma_g^+$)	-51.343 (${}^1\Pi_u$)	-49.954(${}^1\Sigma_g^-$)	-49.700(${}^1\Sigma_u^+$)	-51.142(${}^1\Pi_g$)	-49.906(${}^1\Sigma_u^-$)
	1	-49.478(${}^3\Sigma_g^+$)	-51.134(${}^3\Pi_u$)	-52.084 (${}^3\Sigma_g^-$)	-49.737(${}^3\Sigma_u^+$)	-51.132(${}^3\Pi_g$)	-51.940(${}^3\Sigma_u^-$)
	2	-47.906(${}^5\Sigma_g^+$)	-50.148(${}^5\Pi_u$)	-51.842(${}^5\Sigma_g^-$)	-48.085(${}^5\Sigma_u^+$)	-50.597(${}^5\Pi_g$)	-52.079 (${}^5\Sigma_u^-$)

TABLE II. Natural orbital occupation numbers larger than 0.005 for the lowest-energy states of the $(^3\text{He})_N\text{-Br}_2$ clusters.

	Natural orbital occupation numbers			
	$N=1$	$N=2$	$N=3$	$N=4$
$1\sigma_g^+$	1.000	1.271	0.938	1.090
$2\sigma_g^+$				0.769
$1\pi_u$		0.722	1.687	1.667
$2\pi_u$				0.012
$1\delta_g$			0.305	0.304
$1\phi_u$		0.006	0.070	0.070
$1\sigma_u^+$				0.032
$1\pi_g$				0.042
$1\delta_u$				0.012

values of the occupation numbers reflect the strong He–He correlation and high multiconfigurational character of the corresponding wave functions. Note, however, that the total number of natural orbitals with significant values of η is small. For any cluster size, the sum of η values listed in Table II sums to more than 99.95% of N , while the remaining 0.05% is distributed among more than 167 natural orbitals. This fact indicates the adequacy of the “nuclear orbital” approach of the helium wavefunction used in this work.

In summary, (1) the recently developed JD method has been found to be highly efficient in solving the FCI problem for small doped He clusters; (2) in agreement with previous results, FCI calculations on $(^3\text{He})_N\text{-Br}_2$ clusters result in a high degree of degeneracy for the lowest energy spin states; and (3) the analysis of natural orbital occupation numbers describes the degree of correlation existing in these systems and shows that the helium “nuclear orbital” approach still holds. For larger clusters multiconfigurational self-consistent-field (MCSCF) and/or multireference-CI (MRCI) treatments are probably needed. Very efficient implementations of these methods can be found in MOLPRO.²⁹ However, since the numerical implementations of these methods are based on the standard Davidson’s algorithms, they have failed in our case. Work is in progress to modify the standard MCSCF/MRCI algorithms within MOLPRO by incorporating the JD treatments in order to use them in larger fermionic-doped nanodroplets. Other alternatives to be considered are the coupled-clusters methods which, along with the use of a renormalized (“soft-core”) form of the Hamiltonian, have been successful in nuclear many-body problems.³⁰

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