Quantum Rotation of HCN and DCN in $^4$He

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**Abstract**

We present calculations of rotational absorption spectra of the molecules HCN and DCN in superfluid helium-4, using a combination of the Diffusion Monte Carlo method for ground state properties and an analytic many-body method (Correlated Basis Function theory) for the excited states. Our results agree with the experimentally determined effective moment of inertia which has been obtained from the $J = 0 \to 1$ spectral transition. The correlated basis function analysis shows that, unlike heavy rotors such as OCS, the $J = 2$ and higher rotational excitations of HCN and DCN have high enough energy to strongly couple to rotons, leading to large shifts of the lines and accordingly to anomalous large spectroscopic distortion constants, to the emergence of roton-maxon bands, and to secondary peaks in the absorption spectra for $J = 2$ and $J = 3$.

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I. INTRODUCTION

In microwave helium nanodroplet isolation spectroscopy experiments, Conjusteau et. al. [1] have measured the rotational excitation energy $J = 0 \rightarrow 1$ of HCN and DCN embedded in $^4$He clusters. Their results show a reduction of this excitation energy by factors of 0.815 and 0.827 with respect to gas phase HCN and DCN, respectively. Infrared spectroscopy experiments of HCN by Nauta et. al. [2] yield similar results from analysis of the ro-vibrational excitation of the C-H stretching mode, namely a reduction of 0.795 in the $J = 0 \rightarrow 1$ energy. These fractional reductions are considerably smaller than those observed for heavier molecules such as SF$_6$ and OCS, where reductions by factors of $\sim 0.3$ are seen [3]. The gas phase rotational constants, $B = 1.478222$ cm$^{-1}$ for HCN and $B = 1.207780$ cm$^{-1}$ for DCN, are also much larger than the corresponding values for the heavier molecules (e.g. $B = 0.2029$ cm$^{-1}$ and 0.0911 cm$^{-1}$ for OCS and SF$_6$ respectively). The widely observed reduction in $B$ is understood to be due to the interaction of the molecule with the surrounding $^4$He atoms [4]. For the heavier molecules it has been found that calculations based on the microscopic 2-fluid theory [5] can reproduce the effective rotational constant $B_{\text{eff}}$ [4, 6]. For some heavy linear rotors, a semiclassical hydrodynamical analysis that combines a classical treatment of the molecular rotation with a quantum calculation of helium solvation density approximately reproduced the moment of inertia increase measured in experiments (see table I in Ref. 7), although no agreement is found for the octahedral SF$_6$ molecule [4, 8, 9]. The hydrodynamic contribution to the effective moment of inertia is found to be considerably decreased when the molecular rotation is treated quantum mechanically [10].

These models for heavier molecules are based on analysis of partial or complete adiabatic following of the molecular rotational motion by helium and cannot describe the dynamics of light rotors like HCN and DCN in helium for which adiabatic following does not hold [11]. Furthermore, infrared spectra of HCN [2] and acetylene, C$_2$H$_2$ [12], and other light molecules show a small splitting of the ro-vibrational R(0)-line which cannot be accounted for by these theoretical approaches that focus on the calculation of the helium-induced increase of the moment of inertia. In Ref. 13, a detailed investigation of the effects of the finite $^4$He environment on rotational excitations showed that both hydrodynamic coupling of translational and rotational motion and the anisotropy of the effective interaction between the molecule and the finite $^4$He cluster, can result in splitting of the $R(0)$ spectral line (corresponding to
the $J = 0 \rightarrow 1$ transition) into $M = 0$ and $M = \pm 1$ contributions. However, the observed line shapes could not be explained in the case of HCN, although good agreement was found for the lineshape of the R(0) transition of the heavier rotor OCS.

The molecules HCN and DCN are light rotors, possessing large zero point motion. Therefore, calculation of the ground state already requires a full quantum mechanical treatment of the molecular rotations \[14\]. Furthermore, for the rotational excitations, the spacing between the rotational energy levels is large, of similar magnitude as the roton energy of bulk helium (the roton gap is 8.7K \[15\]). This introduces the possibility of direct coupling between the roton states and the molecular rotational levels of light molecules. The coupling between phonons in $^4$He and molecular rotational levels was analyzed perturbatively in Ref.\[16\], where it was shown that the lower density of phonon states in $^4$He relative to that of particle-hole states in $^3$He leads to a much lower coupling of molecular rotational transitions to excitations of the quantum liquid for the Bose system. This provided a rationale for the observation of sharp rotational lines in infrared molecular spectra in the bosonic $^4$He environment, but not in the fermionic $^3$He environment. The specifics of the dispersion relation in $^4$He were not incorporated in this perturbative analysis. In particular, only a linear phonon spectrum was employed, and the maxon and roton excitations were not taken into account. To allow for the possibility of coupling to maxons and rotons when calculating the response to the motion of these light molecules, it is evident that helium cannot simply be treated as a classical frictionless fluid possessing long wavelength hydrodynamic modes, nor by a quantum fluid possessing quantized phonons with linear dispersion. We must therefore describe the coupled dynamics of the molecule and the strongly correlated helium quantum fluid with true quantum many-body theory, \textit{i.e.}, in principle we must solve the $N + 1$ body Schrödinger equation.

Quantum Monte Carlo is one such fully quantum approach. Zero temperature Quantum Monte Carlo calculations for the rotational motion of a molecule doped into a finite cluster of helium have been carried out successfully for a variety of small molecules \[11, 14, 17, 18\], in which excitation energies have been obtained with the POITSE (Projection operator imaginary time spectral evolution) method \[19\] or similar spectral evolution approaches \[18\]. For HCN in helium clusters, rotational constants $B_{\text{eff}}$ have been obtained for clusters consisting of up to $N = 25$ $^4$He atoms \[14\]. However, in marked contrast to the heavier OCS and SF$_6$ molecules for which the large droplet value is arrived at well before the first solvation shell
(N ≈ 20) is complete [17, 18, 20], convergence to the experimental value of B for HCN in large 4He clusters of several thousands of 4He atoms was not yet found at N = 25. This very different behavior accentuates the distinction between a light and a heavy rotor, and suggests that different physics may underlie the reduction in B for a light molecule. This, combined with the technical difficulties of making POITSE calculations for large clusters and hence to follow the small cluster B value to convergence with increasing size, motivates development of a more analytic approach that is suitable for implementation in the bulk limit. With an analytical approach, implementation is generally simpler in the bulk limit N → ∞ than in a large finite system because of the higher symmetry. However, it is then necessary to recognize that derivation of an analytical model from the N + 1-body Schrödinger equation is necessarily approximative and this may affect the quantitative accuracy of our results.

The method we apply here to the rotational dynamics of HCN in helium (1 linear molecule + N spherical atoms) is a combination of the Correlated Basis Function (CBF) theory (also called (time-dependent) hyper-netted chain / Euler-Lagrange (HNC/EL) method) with diffusion Monte Carlo (DMC) ground state calculations. The CBF method can be formulated as an energy functional approach to solving the many-body Schrödinger equation. In contrast to the formulation of Density Functional Theory (DFT) that is generally applied to helium systems [21, 22], CBF theory eliminates the need for a semi-empirical correlation energy functional by expressing the energy functional not only in terms of the one-body density, but also in terms of pair-densities and, if necessary for quantitative agreement, also of triplet-densities. Similarly to DFT, the stationary version of CBF yields the ground state energy and structure, while the time-dependent extension of CBF yields excited states.

As an analytic approach to the many-body problem, CBF theory requires relatively little computational effort to solve the equations of motion, once these have been derived. The CBF method yields ground state quantities such as the ground state energy, the chemical potentials, and the pair distribution functions. Calculation of excitations in CBF yields not only excitation energies, but also the density-density response function, and from that the dynamic structure function for pure 4He and the absorption spectrum of the dopant molecule, as will be shown explicitly below. Although CBF theory is not an exact method, quantitative agreement has been found for a variety of quantities relevant to 4He systems. These include ground state and collective excitations in bulk 4He [23, 24], excitations in 4He films [25, 26, 27, 28] and clusters [29, 30, 31], and translational motion of atomic impurities
in $^4$He \cite{32}. This generates confidence that CBF theory may allow quantitative calculations of the rotational dynamics of dopant molecules for rotational energies in the range of the phonon-maxon-roton regime. In the case of HCN/DCN, this means for quantum numbers up to $J = 3$. Combining CBF theory for excitations with exact ground state quantities calculated by DMC may also be expected to improve the accuracy of CBF excitations.

In this paper, we restrict ourselves to the simpler case of HCN/DCN in bulk $^4$He, where translational symmetry is preserved and the analytic CBF calculations become correspondingly simpler, as opposed to HCN/DCN in $^4$He clusters. This therefore precludes the calculation of inhomogeneous line-broadening and possible line splitting caused by the inhomogeneous environment of the cluster \cite{13}. The structure of the paper is as follows.

The derivation of the rotation excitation spectrum of a single linear molecule in bulk helium is presented in section II. This analysis is related to the derivation of the translational excitation spectrum of an atom coupling to the phonon-roton excitations in bulk helium, which has been discussed in detail in Ref. 32. In sections II A and II B, we derive the CBF equations for the excitation spectrum of a linear rotor solvated in bulk $^4$He and for its absorption spectrum, respectively. In section II C, we describe how the CBF theory is combined with Diffusion Monte Carlo (DMC) calculations of ground state input quantities in order to obtain excitations and absorption spectra.

In section III we report the DMC results for the ground state quantities for HCN and DCN. Section IV describes the results of the “marriage” of CBF and DMC for rotational excitations. We present and discuss the excitation energies in section IV A and the absorption spectra in section IV B. In a direct analogy with the definition of an effective mass of an effective free particle from the momentum dependence of the excitation energy $E(q)$, it is common to obtain an effective rotational constant $B_{\text{eff}}$ of an effective linear rotor from analysis of one or more spectral transition energies. This was done in Ref. 1 using the experimentally observed $R(0)$ ($J = 0 \rightarrow 1$) spectral line. We present our corresponding results for $B_{\text{eff}}$ obtained from the calculated $J = 0 \rightarrow 1$ transition energies in section IV C. Our calculated values of $B_{\text{eff}}$ are in good agreement with the experimental values, indicating that the reduction in $B_{\text{eff}}$ relative to the gas phase $B$ for these light molecules derives primarily from coupling to the collective modes of $^4$He. This is a very different situation from that for heavier molecules, where the reduction in $B_{\text{eff}}$ derives from coupling to some local helium density that adiabatically follows the molecular rotation \cite{33}, a phenomenon that may
be formally regarded as coupling to $^4$He modes which are localized around the molecule. The present analysis thus indicates that there is indeed a different physics responsible for the reduction in rotational constants for light molecules than for heavy molecules in $^4$He.

A second significant feature of the CBF results is that, although we find that the energy spectrum still has the same symmetry as a linear rotor, i.e., there is no splitting of the $M$ states within a given level in bulk $^4$He, it is evident that nevertheless the $J$ dependence of the rotational energy $E(J)$ deviates considerably from that of an effective rigid linear rotor spectrum, $B_{\text{eff}}J(J+1)$, when a fit of $B_{\text{eff}}$ to more than one $J$ level is made. In particular, we find that the coupling to the roton and maxon collective excitations for higher $J$ levels gives rise to extremely large effective “centrifugal distortion” terms that modify this rigid rotor form. The analysis of this deviation from the rigid rotor spectrum is discussed in detail in section [IV.D].

Lastly, in section [IV.F] we introduce a pseudo-hydrodynamic model that includes only phonon modes of $^4$He but no maxon/roton modes in the CBF calculation. This provides a reference point that allows us to independently assess the effect of the maxon/roton excitations on molecule rotations. The changes in the effective rotational constants $B$ and $D$ relative to the gas phase values deriving from this pseudo-hydrodynamic dispersion model are much reduced relative to the corresponding changes found with the true dispersion curve for $^4$He, and the value of $B_{\text{eff}}$ is no longer in such good agreement with the experimentally measured value ($D_{\text{eff}}$ was not experimentally accessible for HCN in the experiments to date [1, 2]). This provides additional evidence for the critical role of the maxon/roton excitations in the reduction of $B_{\text{eff}}$ for HCN. We summarize and provide conclusions in section [V].

II. THEORY

The CBF method is a microscopic quantum theory for the ground state and excitations of a many-body system. By “microscopic” we mean that there is no input other than the Hamiltonian, and the output quantities are expectation values with respect to the ground state or an excited state, such as energy, density etc. In practice, approximations are necessary in order to render the CBF equations soluble. We will point out these approximations as we introduce them.
In our case the Hamiltonian for \( N \) \(^4\)He atoms with coordinates \( r_i, i = 1, \ldots, N \) and a linear molecule at position \( r_0 \) and orientation \( \Omega = (\theta, \phi) \) in the laboratory frame takes the form

\[
H = B \hat{L}^2 - \frac{\hbar^2}{2M} \nabla_0^2 + \sum_{i=1}^{N} V_X(r_0 - r_i, \Omega) + H_B ,
\]

(2.1)

where \( B \) is the rotational constant of the free linear rotor, \( \hat{L} \) is the angular momentum operator, \( M \) is the mass of the rotor, and \( V_X \) is the molecule–\(^4\)He interaction potential. For HCN-He, we use the 1E8 potential of Atkins and Hutson [34] obtained from fitting to ab initio calculations of Drucker et al. [35]. For DCN-He, we use the same potential (same equilibrium nuclear positions, \( r_{CH} = 1.064\text{Å} \) and \( r_{CN} = 1.156\text{Å} \) [35]) and merely transform the Jacobi coordinates \( (r, \alpha) \) to take into account the change of the center of mass. \( r = |r_0 - r_i| \) is the helium distance from the molecule center of mass, \( \alpha \) is the angle between the vector \( r \) and the molecular axis, measured from the hydrogen end of the molecule.

The operator \( H_B \) is the pure helium Hamiltonian

\[
H_B = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i<j} V_{\text{He}}(|r_i - r_j|) ,
\]

(2.2)

where \( m \) is the mass of an \(^4\)He atom and \( V_{\text{He}} \) is the \(^4\)He–\(^4\)He interaction, for which we use the potential of Ref. 36.

The CBF method has been explained in detail in a number of papers [23, 37, 38, 39, 40, 41], therefore we limit ourselves to giving only a very brief overview here. The starting point is to obtain the ground state wave function of the \( N + 1 \)-body system, here

\[
\Psi_0 = \Psi_0(r_0, r_1, \ldots, r_N, \Omega) .
\]

(2.3)

In the framework of CBF theory, \( \Psi_0 \) is expressed in a Jastrow–Feenberg form, i.e. expressed in terms of correlations:

\[
\Psi_0 = \exp \left[ \frac{1}{2} \sum_{i<j} u_2(r_i, r_j) + \sum_{i<j<k} u_3(r_i, r_j, r_k) + \ldots \right. \left. + \sum_{i=1}^{N} u_X(r_0, r_i, \Omega) + \sum_{i<j} u_X^3(r_0, r_i, r_j, \Omega) + \ldots \right] .
\]

(2.4)

Here the molecule is referred to as \( X \), with center of mass translation coordinate \( r_0 \) and angular orientation \( \Omega \) defined above. The definition of the \( n \)-particle correlations \( u_n \) and \( u_n^X \) is made unique by requiring that \( u_n \) vanishes if one of its coordinates is separated from...
the rest. Furthermore, it provides an exact representation of the ground state when all
correlations up to \( n = N \) are summed, \( i.e. \), up to \( u_N \). However, even for the strongly
correlated \( ^4\)He ground state, correlations between up to just three particles are sufficient to
obtain quantitative agreement of the energy and the pair distribution function \[38\] of bulk
\( ^4\)He with experiments and Monte Carlo simulations. The correlations \( u_n \) are obtained by
solving the Euler-Lagrange equations, which can be written formally as

\[
\frac{\delta E}{\delta u_n(r_1, \ldots, r_n)} = 0 \tag{2.5}
\]

where \( E \) is the expectation value of the Hamiltonian, \( \langle \Psi_0 | H | \Psi_0 \rangle \), and \( n \leq 3 \). The resulting
Euler-Lagrange equations (2.5) are coupled non-linear integro-differential equations and can
be solved iteratively. Derivation of a formulation of equations (2.5) that is appropriate for
numerical solution can be found in Ref. [40]. However, in the present “marriage” of CBF and
DMC, solution of eqns. (2.5) is not necessary since the ground state properties are calculated
by DMC.

A. Excited states

The primary aim of this article is to employ CBF theory in the search for excitations of
the molecule-helium system. The excitations can be obtained by generalizing the ground
state form, Eq. (2.4), to time-dependent correlations, \( i.e. \) \( u_2 = u_2(r_1, r_2; t) \), etc. By allowing
a time-dependent external perturbation potential \( V^{(\text{ext})}(r_0, \Omega; t) \) to act on the molecule, we
can then use linear response theory [42] to obtain excitation energies involving motions of
the molecule. Linear response relies on the knowledge of the ground state, which we assume
to have calculated according to the above recipe or by other means (see section [43]) and
which is then weakly perturbed. The perturbed wave function can therefore be written as

\[
\Psi(t) = \frac{e^{\delta U(t)/2} \Psi_0}{\langle \Psi_0 | e^{\text{Re} \delta U(t)} | \Psi_0 \rangle} \tag{2.6}
\]

where the \textit{excitation operator} \( \delta U(t) \) is given by

\[
\delta U(t) = \delta u_1(r_0, \Omega; t) + \sum_{i=1}^{N} \delta u_2(r_0, r_i, \Omega; t) . \tag{2.7}
\]

Note that we have dropped the \( X \) superscript from the two-particle molecule-helium cor-
relation \( u_2 \). We will continue to do this from here on, using the presence of the molecular
coordinates \( \mathbf{r}_0 \) and \( \Omega \) in \( \delta u_1(\mathbf{r}_0, \Omega; t) \) and \( \delta u_2(\mathbf{r}_0, \mathbf{r}_1, \Omega; t) \) to distinguish helium-molecule from helium-helium correlation terms. Note also that unlike the ground state wave function \( \Psi_0 \), the excited state \( \Psi(t) \) does not possess the translational and rotational symmetry of the full Hamiltonian \( H \). Therefore it is convenient to separate \( \delta U(t) \) into a one-body term \( \delta u_1 \) and 2-body correlations \( \delta u_2 \). Time-dependent correlations between more than 2 particles can also be formally written down and added to Eq. (2.7), but would give rise to numerically intractable equations. Consequently, we restrict ourselves to two-body correlations in \( \delta U(t) \) here.

The two terms in Eq. (2.7) give rise to two Euler-Lagrange equations that are obtained by functional minimization of the action integral

\[
\delta L = \delta \int_{t_1}^{t_2} dt \langle \Psi(t) | H + V^{(\text{ext})}(t) - i\hbar \frac{\partial}{\partial t} | \Psi(t) \rangle = 0 \tag{2.8}
\]

with respect to \( \delta u_1 \) and \( \delta u_2 \). The action integral of an spherical impurity (\(^3\)He and atomic hydrogen) in bulk \(^4\)He can be found in Refs. 32 and 43. We shall refer to this reference integral for a spherical impurity as \( L_0 \). For a linear molecule in helium, the situation is complicated (i) by the additional rotational kinetic energy term in the Hamiltonian,

\[
H_0^{\text{rot}} = BL^2 = -B \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right), \tag{2.9}
\]

and (ii) by the breaking of the rotational symmetry of the ground state distribution of \(^4\)He atoms around the molecule. Similarly to the derivation of \( L_0 \) [32], we find for the expansion of \( \mathcal{L} \) to second order in \( \delta U \):

\[
\mathcal{L} = \mathcal{L}_0 + \frac{1}{4} B \int_{t_1}^{t_2} dt \left\{ \int d\Omega d\Omega' \rho^X \left[ |\partial_\theta \delta u_1(0, \Omega)|^2 + \frac{|\partial_\phi \delta u_1(0, \Omega)|^2}{\sin^2 \theta} \right] \\
+ \int d\Omega d\Omega' d\Omega'' \rho_2(0,1,\Omega') \left[ (\partial_\theta \delta u_1^*(0, \Omega)) (\partial_\phi \delta u_2(0, 1, \Omega)) \right] + c.c \\
+ \left( \frac{\partial_\phi \delta u_1^*(0, \Omega)}{\sin \theta} \right) \left( \frac{\partial_\phi \delta u_2(0, 1, \Omega)}{\sin \theta} \right) + c.c + |\partial_\phi \delta u_2(0, 1, \Omega)|^2 + \frac{|\partial_\phi \delta u_2(0, 1, \Omega)|^2}{\sin^2 \theta} \left] \right\} \\
+ \int d\Omega d\Omega' d\Omega'' d\Omega''' \rho_3(0,1,2,\Omega') \left[ (\partial_\theta \delta u_1^*(0, \Omega)) (\partial_\phi \delta u_2(0, 2, \Omega)) \right] + c.c \\
+ \left( \frac{\partial_\phi \delta u_1^*(0, \Omega)}{\sin \theta} \right) \left( \frac{\partial_\phi \delta u_2(0, 2, \Omega)}{\sin \theta} \right) \right\} \\
+ \int_{t_1}^{t_2} dt \int d\Omega \rho_1[\delta U](0, \Omega) V^{(\text{ext})}(0, \Omega),
\]

where for simplicity we abbreviated the functional arguments \( \mathbf{r}_i \) by \( i \), and have omitted the time argument. \( \rho_2(0,1,\Omega) \) and \( \rho_3(0,1,2,\Omega) \) are the ground state probability densities of one
and two $^4$He atoms around the molecule, respectively, defined as

$$\rho_2(0, 1, \Omega) = \frac{N}{\mathcal{N}} \int d2 \ldots dN |\Psi_0(0, 1, \ldots, N, \Omega)|^2$$

$$\rho_2(0, 1, 2, \Omega) = \frac{N(N-1)}{N} \int d3 \ldots dN |\Psi_0(0, 1, \ldots, N, \Omega)|^2,$$

where $\mathcal{N}$ is the normalization integral of $\Psi_0$.

$$\rho_1[\delta U](0, \Omega) = \rho^X + \Re \delta \tilde{\rho}_1(0, \Omega)$$

is the time-dependent probability density of the molecule expanded to first order in $\delta U$, where we have defined the complex density fluctuation

$$\delta \tilde{\rho}_1(0, \Omega) = \rho^X \delta u_1(0, \Omega) + \int d1 \rho_2(0, 1, \Omega) \delta u_2(0, 1, \Omega),$$

and $\rho^X = 1/V$ and $\rho = N/V$ are the constant ground state densities of the molecule and of the $^4$He atoms, respectively, in the normalization volume $V$.

The Euler-Lagrange equations $\delta \mathcal{L}$, i.e. the 1-body and 2-body equations

$$\frac{\delta \mathcal{L}}{\delta u_1^*(r_0, \Omega)} = 0,$$

$$\frac{\delta \mathcal{L}}{\delta u_2^*(r_0, r_1, \Omega)} = 0,$$

describe the time-dependent response of the system to the perturbation $V^{(\text{ext})}$. The linear response is obtained by linearizing the equations in terms of the corresponding correlation fluctuations $\delta u_1$ and $\delta u_2$. In the following, we bring these equations into a form where the time-dependent density fluctuation $\delta \rho_1(0, \Omega)$ is a linear functional of $V^{(\text{ext})}$. From that, excitations are derived by setting $V^{(\text{ext})} = 0$.

We first eliminate $\delta u_1(0, \Omega)$ in favor of the (complex) one-body density fluctuation eq. (2.13). Then the linearized 1-body equation of motion can be written

$$B \frac{1}{\sin \theta} \left( \frac{\partial}{\partial \theta} \right) \cdot \mathbf{j}^r(0, \Omega) + i \delta \tilde{\rho}_1(0, \Omega) + \nabla_d \mathbf{j}^X(0, \Omega) - 2V^{(\text{ext})}(0, \Omega) = 0,$$

where weak $V^{(\text{ext})}$ is any perturbation acting only on the molecular degrees of freedom and $\mathbf{j}^X$ is the translational current fluctuation. This is defined in Ref. 32 and need not concern us for rotational excitations, as we will see explicitly below. In analogy to $\mathbf{j}^X$, we have defined the “rotational” current fluctuation

$$\mathbf{j}^r(0, \Omega) = \left( \frac{\sin \theta}{\sin \theta} \frac{\partial}{\partial \phi} \right) \delta \tilde{\rho}_1(0, \Omega) - \int d2 \delta u_2(0, 2, \Omega) \left( \frac{\sin \theta}{\sin \theta} \frac{\partial}{\partial \phi} \right) \rho_2(0, 2, \Omega).$$
\( \delta \rho_1 (0, \Omega) \) is the time-dependent density fluctuation defined in eq. (2.13), while, due to the linearization, \( \rho_2 (0, 2, \Omega) \) is the ground state pair density. The second and third terms of eq. (2.15) stem from the variation \( \delta \mathcal{L}_0 / \delta u^*_2 (0, \Omega) \). The density fluctuation \( \delta \tilde{\rho}_1 \) couples via \( j^r \) and \( j^X \) to the 2-body equation in eq. (2.14). The 2-body equation is more lengthy:

\[
0 = \frac{B}{\sin \theta} \sin \rho_2 (0, 1, \Omega) \partial_\theta \frac{\delta \tilde{\rho}_1 (0, \Omega)}{\rho^X} + \frac{B}{\sin^2 \theta} \partial_\phi \rho_2 (0, 1, \Omega) \partial_\phi \frac{\delta \tilde{\rho}_1 (0, \Omega)}{\rho^X} \tag{2.17} \\
+ \int d^2 \frac{B}{\sin \theta} \sin \theta \rho_3 (0, 1, 2, \Omega) \partial_\theta \delta u_2 (0, 1, \Omega) + \int d^2 \frac{B}{\sin^2 \theta} \partial_\phi \partial_\theta \rho_3 (0, 1, 2, \Omega) \partial_\phi \delta u_2 (0, 1, \Omega) \\
- \int d^2 \frac{1}{\rho^X} \sin \theta \rho_2 (0, 1, \Omega) \partial_\theta \rho_2 (0, 2, \Omega) \delta u_2 (0, 1, \Omega) \\
- \int d^2 \frac{1}{\rho^X} \sin^2 \theta \partial_\phi \rho_2 (0, 1, \Omega) \delta u_2 (0, 1, \Omega) \\
+ i \hbar \rho \tilde{\rho}_2 (0, 1, \Omega) + \nabla_1 \cdot \mathbf{J}_2 (0, 1, \Omega) - \frac{\delta \mathcal{L}^{\text{trans}}_0}{\delta u^*_2 (0, 1, \Omega)} - 2 \rho_2 (0, 1, \Omega) V^{(\text{ext})} (0, \Omega).
\]

\( \delta \mathcal{L}^{\text{trans}}_0 / \delta u^*_2 (0, 1, \Omega) \) represents the terms related to the translational degrees of freedom of the molecule, the derivation of which can be found in Ref. 32. The (complex) 2-body density fluctuation \( \delta \tilde{\rho}_2 (0, 1, \Omega) \) can be expressed as a functional of \( \delta \tilde{\rho}_1 (0, \Omega) \) and \( \delta u_2 (0, 1, \Omega) \):

\[
\delta \tilde{\rho}_2 (0, 1, \Omega) = \rho_2 (0, 1, \Omega) \frac{\delta \tilde{\rho}_1 (0, \Omega)}{\rho^X} + \rho_2 (0, 1, \Omega) \delta u_2 (0, 1, \Omega) \\
+ \int d^2 \left( \rho_3 (0, 1, 2, \Omega) - \frac{1}{\rho^X} \rho_2 (0, 1, \Omega) \rho_2 (0, 2, \Omega) \right) \delta u_2 (0, 2, \Omega),
\]

which follows from the definition (2.10). The \(^4\text{He}\)-current fluctuation \( \mathbf{J}_2 \) induced by the rotating molecule is defined as

\[
\mathbf{J}_2 (0, 1, \Omega) = \frac{\hbar}{2m} \rho_2 (0, 1, \Omega) \nabla_1 \delta u_2 (0, 1, \Omega).
\tag{2.19}
\]

Unfortunately, solution of the coupled set of equations (2.15) and (2.17) is not feasible without further approximations to the 2-body equation (2.17). In a rather drastic approximation step, we therefore expand the pair distribution

\[
g (0, 1, \Omega) = \frac{\rho_2 (0, 1, \Omega)}{\rho^X \rho}
\tag{2.20}
\]

about unity. This is commonly referred to as the “uniform limit” approximation [37]. It has the advantage of leading to a particularly simple expression for the excitation energies in terms of a self energy correction, and has been used in many CBF calculations of excited
states of $^4\text{He}$ and impurities in $^4\text{He}$. Therefore, this uniform limit approximation is our first candidate for simplifying eq. (2.17). We discuss the extent of the validity of this approximation in section III where we present our DMC result for $g$.

When applied to the equations of motions (2.15) and (2.17), the uniform limit approximation amounts to replacing the pair distribution function $g(0,1,\Omega)$ by unity in coordinate space, but not in integrals, where it is retained in full form. The triplet density in the uniform limit approximation then reads

$$
\rho_3(0,1,2,\Omega) - \frac{1}{\rho^X}\rho_2(0,1,\Omega)\rho_2(0,2,\Omega) \approx \rho^X\rho (g(1,2) - 1),
$$

(2.21)

where $g$ is the pair distribution of two $^4\text{He}$ atoms, regardless of the position $r_0$ of the molecule. We can furthermore eliminate $\delta \tilde{\rho}_2(0,1,\Omega)$ by $\delta \rho_1(0,\Omega)$ and $\delta u_2$, using eq. (2.18), and then make use of the 1-body equation (2.16), in order to arrive at

$$
0 = B(\partial_\theta \tilde{\rho}_1(0,\Omega)\rho^X) - B\frac{1}{\sin^2\theta}(\partial_\theta \rho \tilde{\rho}_1(0,\Omega)\rho^X)(\partial_\theta \rho_2(0,1,\Omega))
$$

(2.22)

+ $\rho^X\int d2 S(1,2) BL^2\delta u_2(0,2,\Omega) + \rho^X\rho \frac{\hbar^2}{2m}\nabla^2\delta u_2(0,1,\Omega)$

+ $\frac{\hbar^2}{2M}(\nabla_0\tilde{\rho}_1(0,\Omega)\rho^X)(\nabla_0\rho_2(0,1,\Omega)) - \rho^X\rho \frac{\hbar^2}{2M}\int d2 S(1,2)\nabla^2_0\delta u_2(0,2,\Omega)$

+ $i\hbar\rho^X\int d2 S(1,2)\delta u_2(0,2,\Omega),$

where the terms involving $\nabla_0$ stem from $\delta C_0^\text{trans}/\delta u_2^*(0,1,\Omega)$. Note that the explicit reference to the external field $V^{(\text{ext})}(0,\Omega)$ has now been eliminated. This means that the 2-body correlation fluctuations are only driven by the 1-body correlation fluctuations, which in turn are the response to $V^{(\text{ext})}(0,\Omega)$. In the above equation, $S$ is the static structure function of $^4\text{He}$ in coordinate space,

$$
S(|r_1 - r_2|) = \sigma(r_1 - r_2) + \rho (g(|r_1 - r_2|) - 1),
$$

(2.23)

$$
S(k) = \int d^3 r e^{ikr} S(r).
$$

(2.24)

The equations (2.15) and (2.22) can now be solved by expansion in plane waves and spherical harmonics. We define

$$
\delta \rho_1(r_0,\Omega) = \sum_{J,M} \int \frac{d^3 q}{(2\pi)^3} e^{iqr} Y_{JM}(\Omega) \delta \tilde{\rho}_{JM}(q)
$$

(2.25)

and

$$
V^{(\text{ext})}(r_0,\Omega) = \sum_{J,M} \int \frac{d^3 q}{(2\pi)^3} e^{iqr} Y_{JM}(\Omega) V^{(\text{ext})}_{JM}(q)
$$

(2.26)
\[ \delta u_2(\mathbf{r}_0, \mathbf{r}_1, \Omega) = \sum_{\ell, m} \int \frac{d^3k}{(2\pi)^3} \frac{d^3p}{(2\pi)^3} e^{i\mathbf{k}\cdot\mathbf{r}_0} e^{i\mathbf{p}\cdot(\mathbf{r}_0-\mathbf{r}_1)} Y_{\ell m}(\Omega) \alpha_{\ell m}(\mathbf{k}, \mathbf{p}) \] (2.27)

\[ g(\mathbf{r}_0, \mathbf{r}_1, \Omega) - 1 = g(r, \cos \alpha) - 1 = 4\pi \sum_{\ell} (2\ell + 1) P_{\ell}(\cos \alpha) \int \frac{dkk^2}{(2\pi)^3} j_\ell(kr) g_\ell(k) \] (2.28)

where \( \mathbf{r} = \mathbf{r}_0 - \mathbf{r}_1 \) and \( \cos \alpha = \mathbf{r} \cdot \Omega \).

If we restrict ourselves to an external perturbation potential that couples only to the rotational degree of freedom, i.e. \( V_{\ell m}^{(\text{ext})}(q) = 0 = V_{\ell m}^{(\text{ext})} \), then translational motion is not directly excited. Since in CBF theory the molecule+helium system is regarded as being in its ground state before excitation, we are therefore calculating only the purely rotationally excited states, i.e. \( \delta \tilde{\rho}_{\ell,m}(q = 0) \equiv \delta \tilde{\rho}_{\ell,m} \).

With the above transformations and after transforming from time to frequency, the 1-body and 2-body response equations (2.15) and (2.22) become coupled algebraic equations. Eq. (2.15) becomes

\[ \hbar \omega \delta \tilde{\rho}_{JM} (\omega) + 2 V_{JM}^{(\text{ext})}(\omega) = BJ(J+1) \delta \tilde{\rho}_{JM} + \]

\[ + 4\pi \rho X \rho B \sum_{\ell', m'} (-i)^{\ell'} \int \frac{d^3p}{(2\pi)^3} Y_{\ell'm'}^* (\Omega - p) g_\ell(p) \alpha_{\ell m}(0, \mathbf{p}; \omega) (-1)^M \left\langle J \quad \ell' \quad \ell \right| -M \cdot m' \cdot m \right\rangle \]

(2.29)

where we note that the translational current fluctuation \( \mathbf{j}_X \) in eq. (2.15) vanishes. Eq. (2.22) becomes

\[ (B\ell(\ell + 1) + \frac{\hbar^2 p^2}{2m S(p)} + \frac{\hbar^2 p^2}{2M} - \hbar \omega) \alpha_{\ell m}(0, \mathbf{p}; \omega) = \]

\[ -4\pi B \sum_{\lambda', \mu'} (-i)^{\lambda'} (1)^m \left\langle \lambda \quad \lambda' \quad \ell \right| \mu \quad \mu' \quad -m \right\rangle Y_{\lambda' \mu'}^* (\Omega_p) \frac{\delta \tilde{\rho}_{\lambda \mu}(\omega)}{\rho^X} g_\lambda(p) S(p) \].

Here the static structure factor \( S(p) \) is defined in eq. (2.24). The energy expression on the left hand side of eq. (2.30) contains the free linear rotor spectrum \( B\ell(\ell + 1) \) and the Bijl-Feynman spectrum [44] of bulk \(^4\text{He}\),

\[ \epsilon(p) = \frac{\hbar^2 p^2}{2m S(p)} \].

The symbols in the angular brackets follow from angular integration of spherical harmonics

\[ \left\langle \ell_1 \quad \ell_2 \quad \ell_3 \right| m_1 \quad m_2 \quad m_3 \left\rangle = \sqrt{\tilde{L}(\ell_1, \ell_2, \ell_3)} \left( \ell_1 \quad \ell_2 \quad \ell_3 \right| m_1 \quad m_2 \quad m_3 \right) \]

\[ \tilde{L}(\ell_1, \ell_2, \ell_3) = \frac{1}{4} \tilde{L}(\ell_1, \ell_2, \ell_3) \left( \ell_1(\ell_1 + 1) + \ell_2(\ell_2 + 1) - \ell_3(\ell_3 + 1) \right)^2 \] (2.31)

\[ \tilde{L}(\ell_1, \ell_2, \ell_3) = \frac{(2\ell_1 + 1)(2\ell_2 + 1)(2\ell_3 + 1)}{4\pi} \left( \ell_1 \quad \ell_2 \quad \ell_3 \right| 0 \quad 0 \quad 0 \right)^2 \].

13
The expressions in round brackets are Wigner’s 3-$j$ symbols \[45\]. After eliminating $\alpha_{\ell m}(0, \mathbf{p})$ in eq. (2.29) by using eq. (2.30), we use the summation rules for the Wigner 3-$j$ symbols to further simplify eq. (2.29). It turns out that most of the angular quantum number summations are trivial and that the $\delta \tilde{\rho}_{JM}$ coefficients do not mix. This leads to the simple formula

\[
(BJ(J + 1) + \Sigma_J(\omega) - \hbar \omega) \delta \tilde{\rho}_{JM}(\omega) = 2V_{JM}^{(\text{ext})}(\omega) .
\] (2.32)

Hence we have found the linear response of the density, $\delta \tilde{\rho}_{JM}$, to a weak perturbation of symmetry $(J, M)$, $V_{JM}^{(\text{ext})}$. The excitation energies of the system are obtained by setting the perturbation potential to zero and solving eq. (2.32),

\[
\hbar \omega = BJ(J + 1) + \Sigma_J(\omega) .
\] (2.33)

This has to be solved self-consistently in order to obtain the excitation energy $\omega_J$ for given $J$ (or energies, if there exist more than one solution for given $J$). These solutions correspond to the energies $E_J = \hbar \omega_J$ of the coupled molecule-helium system, in the usual spectroscopic notation with $J$ the total angular momentum associated with the solvated molecule. $\Sigma_J(\omega)$ is the self energy

\[
\Sigma_J(\omega) = -B^2(4\pi)^2 \rho \sum_{\ell} \int \frac{dp}{(2\pi)^3} \frac{p^2}{S(p)} \frac{\sum_{\ell'} \tilde{L}(J, \ell', \ell) g_{\ell'}^2(p)}{B\ell(\ell + 1) + \epsilon(p) + \hbar^2p^2/2M - \hbar \omega} .
\] (2.34)

We note that $\Sigma_J(\omega)$ does not depend on the quantum number $M$ anymore, and that therefore we will not observe any $M$-splitting of the R(0) line of HCN in bulk $^4$He. This splitting has been found in spectra of HCN in $^4$He droplets as reported in Ref. 2, where it has been attributed to the finite size of the droplets$^{13}$. Our result for the excitation energy, eq. (2.33), indicates that all $M$-levels are degenerate when HCN is embedded in uniform bulk $^4$He. Note that infrared spectra of HCN solvated in $^4$He droplets in a strong electric field show clear evidence of $M$-splitting \[2\]. The lack of $M$-splitting in our calculation of HCN in the homogeneous environment of bulk $^4$He thus indicates that the inhomogeneous environment of finite $^4$He droplets may indeed be responsible for the observed spectral splitting.

In general, the self energy will be complex. Strictly speaking, eq. (2.33) cannot be solved self-consistently in that case, and we can only speak in terms of the response of the system to the perturbation (i.e. laser field). The imaginary part of $\Sigma_J(\omega)$, which is the homogeneous line-width, i.e. the inverse life-time of the state $J$, results from the contour integration $\int dp$ when the energy denominator has a zero. At such quantum numbers $p$ and $\ell$, energy
conservation allows for a decay of state $J$ having energy $\hbar \omega_J$ into a lower rotational excitation with energy $B\ell(\ell + 1)$, while exciting a phonon of energy $\epsilon(p)$ and translational motion of the molecule of energy $\hbar^2 p^2/2M$ (momentum conservation) such that $\hbar \omega_J = B\ell(\ell + 1) + \epsilon(p) + \hbar^2 p^2/2M$. For all other combinations of $p$ and $\ell$, a decay would not conserve energy. These decay channels are closed.

The quantity $\tilde{L}$ \eqref{eq:2.31} contains a Wigner 3-$j$ symbol as well as a rotational kinetic energy factor (the expression in the round brackets on the lhs of eq. \ref{eq:2.31}). Combined, they obviously lead to the selection rules

$$
\tilde{L}(\ell_1, \ell_2, \ell_3) = 0, \text{ if } \ell_1 + \ell_2 + \ell_3 \text{ uneven }
$$

$$
\tilde{L}(\ell_1, \ell_2, \ell_3) = 0, \text{ if } \ell_1, \ell_2, \ell_3 \text{ cannot form a triangle}
$$

$$
\tilde{L}(\ell_1, \ell_2, \ell_3) = 0, \text{ if } \ell_1 = 0 \text{ or } \ell_2 = 0.
$$

It follows that $\Sigma_J(\omega) = 0$ for $J = 0$, i.e. the self energy does not renormalize the ground state energy. The coupling of the spectra in the energy denominator is mediated by the anisotropic pair probability distribution $g(r, \cos \alpha)$, decomposed into its Legendre expansion coefficients. Furthermore, the spherical expansion coefficient $g_{\ell' = 0}$ does not contribute to $\Sigma_J(\omega)$.

We note that in the self energy part of the spectrum \eqref{eq:2.33}, $\hbar \omega_J$ couples to free rotor states, to the free translational states, and to the Bijl-Feynman spectrum of helium. Although we should not over-interpret the meaning of the individual terms in $\Sigma_J(\omega)$, in an exact expression for the correction to the rotational energy in the helium environment we would expect to find a coupling to renormalized molecular rotations and translations. We would also expect to see coupling to the exact energy spectrum of $^4$He, instead of to the Bijl-Feynman spectrum. Going beyond the uniform limit approximation for the probability densities might improve the molecular rotation spectrum in these respects, as has been found for other excitations in helium. These include calculations of the bulk helium spectrum \cite{24} and of the effective mass of $^3$He impurities in $^4$He \cite{46}. Alternatively (and much easier), we can choose a phenomenological approach and try to improve the self energy of eq. \ref{eq:2.33} by using any one or a combination of the following replacements in the energy denominator of the self energy:

1. In the following, we will always use the experimentally measured excitation spectrum instead of the Bijl-Feynman spectrum.
2. We can use the dispersion of translational motion of HCN and DCN in bulk $^4$He, $\hbar^2 p^2/2M_{\text{eff}}$ instead of the free dispersion. Since we don’t know of any experimental value for $M_{\text{eff}}$ (which would be a tensor quantity), we use the bare mass $M$.

3. We can use $\hbar\omega_\ell$ self-consistently instead of $B\ell(\ell+1)$. In this case, we solve $\hbar\omega = B\ell(\ell+1) + \Sigma_\ell(\omega)$ for $\hbar\omega$ angular quantum number $\ell$, and the solution $\hbar\omega_\ell$ replaces $B\ell(\ell+1)$ in the energy denominator of $\Sigma_J(\omega)$ for the next iteration; the procedure is iterated until convergence is reached for all $\hbar\omega_J$. In the case of the calculation of the effective mass of impurities in $^4$He, this phenomenological approach was shown to to improve agreement with experimental results [32]. However, we will see that in case for molecule rotations in $^4$He, for given $J$ we can have several solutions $\omega_J$ of eq. (2.33), see appendix A. We minimize the ambivalence associated with this procedure and will not use this phenomenological improvement of the self energy.

We discuss the dependence of the results on these phenomenological “improvements” in appendix C where $B_{\text{eff}}/B_0$ is calculated for various combinations of replacements 1, 2, and 3. For the rest of the paper, we apply only replacement 1.

A related concern is the missing of decay channels where localized $^4$He excitations are generated instead of a bulk helium excitation $\epsilon(p)$. Localized layer phonons and rotons have been calculated [47] and observed [48] for helium adsorbed to graphite sheets, and localized vibrations calculated for helium adsorption on aromatic molecules [49]. Since the rotation of a molecule in $^4$He involves a correlated motion of the molecule and the surrounding $^4$He atoms, it can be regarded as involving a localized “layer” excitation of the $^4$He when observed from the molecule frame. One significant difference from layer excitations of helium adsorbed to an extended substrate is that here the molecule “substrate” is so light that its motion must be taken into account (the rotational motion has been seen to have an influence on the vibrational energies for $^4$He adsorbed on the benzene molecule [49]). However, decay into channels other than bulk helium excitations, such as the localized molecule-helium excitations themselves, is beyond the ansatz of eq. (2.7) and the uniform limit approximation, as we have pointed out above. Deriving and solving the CBF equations in the frame of the molecule would allow coupling to localized excitations, although it would considerably complicate the CBF equations. An extension in this direction might allow analysis of the rotational dynamics of heavier molecules such as OCS and extraction of the
moment of inertia renormalization deriving from coupling to some adiabatically following helium [4]. However, for the light HCN molecule, our results below show good agreement with the experimental rotational constant in helium, indicating that such coupling to localized excitations is not important in this case.

B. Linear Response and absorption spectrum

Once we have derived the excitation energy of molecular rotations in $^4\text{He}$ from a linear response approach, we can also obtain the dynamic response function $\chi(\omega)$, which is the linear operator relating a weak perturbation $V^{(\text{ext})}$ of frequency $\omega$ and the response of the probability density $\delta \rho_1$:

$$\delta \rho_1(\omega) = \chi(\omega) V^{(\text{ext})}(\omega).$$

$\chi(\omega) = \chi'(\omega) + i\chi''(\omega)$ consists of a real part $\chi'(\omega)$ describing dispersion, and an imaginary part $\chi''(\omega) \equiv S(\omega)$ describing absorption [42, 50] (note that our definition of $S(\omega)$ differs by a factor of $\pi$ from the definition of Ref. 42). However, we cannot simply identify the inverse of the expression in the bracket in eq. (2.32) with $\chi(\omega)$, because $\delta \tilde{\rho}(\omega)$ is the Fourier transform of the complex density fluctuation $\delta \tilde{\rho}_1(0, \Omega)$. The physical density response in linear order is given by the real part of $\delta \tilde{\rho}_1(0, \Omega)$:

$$\delta \rho_1(0, \Omega, t) \equiv \langle \Phi(t)|\hat{\rho}_1(0, \Omega)|\Phi(t)\rangle = \Re \delta \tilde{\rho}_1(0, \Omega, t).$$

Here $\hat{\rho}_1(r_0, \Omega)$ is the molecule density operator, which is given in coordinate space by $\delta(r_0 - r')\delta(\Omega - \Omega')$. The expectation value of $\hat{\rho}_1(0, \Omega)$ is the probability to find a molecule at position $r_0$ and orientation $\Omega$.

To obtain $\chi(\omega)$ from eq. (2.32), we first note that

$$\delta \rho_{JM}(\omega) = \frac{1}{2}[\delta \tilde{\rho}_{JM}(\omega) + (-1)^M \delta \tilde{\rho}_{J,-M}^*(-\omega)]$$

$$\left(V_{J,-M}^{(\text{ext})}(\omega)\right)^* = (-1)^M V_{JM}^{(\text{ext})}(\omega),$$

where we used the fact that $V^{(\text{ext})}(\Omega, t)$ is real. With relation (2.32) we find

$$\delta \rho_{JM}(\omega) = [G_J(\omega) + G_J^*(-\omega)] V_{JM}^{(\text{ext})}(\omega),$$

where $G_J(\omega)$ is the resolvent

$$G_J(\omega) = [BJ(J + 1) + \Sigma_J(\omega) - \hbar \omega]^{-1}. \quad (2.36)$$
Since $G_J(\omega)$ is real for $\omega < 0$, we obtain for the dynamic response function

$$\chi_J(\omega) = G_J(\omega) + G_J(-\omega). \quad (2.37)$$

From this the absorption spectrum of a rigid linear rotor exposed to dipole ($J = 1$), quadrupole ($J = 2$) etc. radiation of frequency $\omega$ can be obtained as

$$S_J(\omega) = \Im m \chi_J(\omega) = \Im m G_J(\omega). \quad (2.38)$$

C. Marriage of DMC and CBF

Formulations of the ground state Euler-Lagrange equations (2.5) which are suitable for numerical solution have to take advantage of the symmetries of the system under consideration. In our case this means translational symmetry and rotational symmetry around the axis of the linear molecule. Unlike the corresponding CBF calculation of excitation (2.14), the ground state equations (2.5) cannot be linearized, due to the strongly repulsive interactions. Consequently both their formulation for a specific symmetry and their numerical solution, are more demanding than the calculation of excitations. Nevertheless, the calculation of the self energy $\Sigma_J(\omega)$ (2.34) does require knowledge of some ground state quantities, in particular of the $^4\text{He}^-^4\text{He}$ and the $^4\text{He}$–molecule pair distribution functions $g(1,2)$ (eq. (2.23)) and of $g(0,1,\Omega)$ (eq. 2.20).

The $^4\text{He}^-^4\text{He}$ pair distribution function $g(1,2)$ is the Fourier transform of the static structure factor $S(k)$. For bulk $^4\text{He}$ this has been obtained with great accuracy from neutron scattering experiments [51, 52]. $S(k)$ has also been calculated using hypernetted chain / Euler-Lagrange theory (HCN/EL) [32] and DMC. We have used the $S(k)$ at $T = 0K$ from Ref. 32 as well as the experimentally determined $S(k)$ at $T = 1K$ from Ref. 51. These give essentially identical results for the rotational excitation energies, i.e. the results are independent of the finer details of $S(k)$. We note that doping $N$ $^4\text{He}$ atoms with a single molecule will cause only a change of $S(k)$ on the order of $O(1/N)$. Therefore we can safely use the $S(k)$ of pure $^4\text{He}$ in the expression for the self energy (2.34).

We additionally need to calculate the $^4\text{He}$–molecule pair distribution function $g(0,1,\Omega)$. Here Diffusion Monte Carlo (DMC) is of use: DMC is easy to implement for the calculation of ground state properties, and since it does not require prior specification of symmetries, one DMC implementation can be applied to any molecule-$^4\text{He}$ system with only
little modification. Hence we shall employ DMC for calculation of the ground states instead of solving equations (2.3). This effectively avoids the difficulties of solving the non-linear Euler-Lagrange equations in a ground state calculation. We therefore use CBF theory only for excited states. The combined procedure can be summarized as follows:

**Step 1:** DMC for calculation of the $^4$He-molecule pair distribution $g(0,1,\Omega)$;

**Step 2:** CBF for calculation of rotational excitations $\hbar\omega_J$ and the corresponding absorption spectrum, using as input the $^4$He-molecule pair distribution $g(0,1,\Omega)$ obtained in step 1 and the $^4$He-$^4$He pair distribution taken from experimental neutron scattering data [15, 54].

The energies $\hbar\omega_J$ reported for HCN and DCN in this work (section IV A) are obtained using these two steps.

In addition to the approximate calculation of excitation energies and life-times, CBF provides us with calculation of an excitation operator $\delta U$ for which $\delta U|\Phi_0\rangle$ is a good approximation of the excited state wave function. This raises a potentially useful option for further improvement of energy calculations in these systems by direct means. We note that the representation of an excited state in terms of an excitation operator that is made in CBF is conceptually similar to the representation made in the POITSE approach [19]. In POITSE, the excitation operator provide input for a zero temperature imaginary time correlation function calculation from which the corresponding excitation energy is obtained by inverse Laplace transformation. In CBF, the excitation operator is one of the outputs of the calculation, and it is normally discarded. Finding the appropriate excitation operator for a POITSE calculation can be a hard problem in some systems. Therefore, knowledge of a good excitation operator deriving from a high quality CBF calculation may help considerably in reducing the computational expense as well as in simplifying the inverse Laplace transformation of a POITSE calculation. By using equations (2.13), (2.27), and (2.30) one can show that within CBF the 1-body term of $\delta U$ in Eq. (2.7) is proportional to

$$\delta u_1(\Omega) \sim Y_{JM}(\Omega)$$

i.e. the free rotor wave function, corresponding to an excitation energy $BJ(J+1)$. Thus, it is the 2-body terms of $\delta U$ which are responsible for the reduction in value of effective rotational constant $B_{\text{eff}}$ below the free rotor value $B$. To date, POITSE and related calculations for
rotational excitations of molecules in helium clusters \cite{14, 17, 18, 55} have used only 1-body excitation operators of the above form. We therefore propose that in future implementations of spectral evolution methods such as POITSE, one employ the CBF excitation operator $\delta U$ of Eq. (2.7). In this situation, the output of CBF, $\delta U$, may then be used as the input to a third calculation step, namely

**Step 3:** CBF provides the excitation operator for a POITSE calculation of the exact excitation energies $\hbar \omega_J$.

We expect that because of the incorporation of molecule-helium correlations into the excitation operator within an exact calculation methodology, this should provide an improvement over the present calculations that terminate after step 2.

**III. RESULTS: GROUND STATE**

The implementation of DMC for a single linear molecule surrounded by $^4$He follows \cite{56, 57}, treating the molecule as a rigid body with both, rotational and translational degrees of freedom. The difference is that here the system is confined to a simulation box of appropriate size and periodic boundary conditions are applied. The simulation box moves with the molecule such that the latter is kept in the center of the box (but the box does not rotate with the molecule). The size $s$ of the simulation box can be either adjusted such that (i) the system consisting of 256 $^4$He atoms and a single HCN or DCN molecule are in equilibrium, *i.e.* that the ground state energy is minimized with respect to variations of the box size; or such that (ii) the $^4$He density reaches the asymptotic equilibrium value $\rho = 0.022\text{Å}^{-3}$ furthest away from the molecule (the edge of the simulation box). In the first method, the calculated quantity (the total energy) changes quadratically with the change of $s$, and in the second method the calculated quantity (the asymptotic density) changes linearly. The first method is thus more susceptible to errors by construction. The uncertainty in the total energy is largely due to the cut-off of the $^4$He-$^4$He interaction potential at large distances (see below). For this reason, we chose to adjust $s$ by the second method. In order to avoid excessive amount of calculations to find the equilibrium density (zero pressure), we choose only 3 box sizes, $s = 22.5\text{Å}, 23.0\text{Å},$ and $23.5\text{Å}$. We found that the $s = 23.0\text{Å}$ simulation yields edge densities closest to the equilibrium bulk value. Using one of the other box sizes did
not change our results for the rotational excitation energies within the statistical error. We have used a time step of \( dt = 0.15 \text{ mK} \) for the imaginary-time evolution to the ground state. We have doubled \( dt \) and again have obtained the same result for the rotational excitation energies, thereby verifying that the DMC energies are free of finite time step bias.

Ground state expectation values (\( i.e. \ g(r, \cos \alpha) \)) have been calculated with pure estimators using descendant weighting of importance sampled DMC according to the approach of Ref. 58. The trial wave function used here for the importance sampled DMC has the form

\[
\Psi_T = \exp \left[ \frac{1}{2} \left( \sum_{i=1}^{N} u_1^{(T)}(|r_i - r_0|, \cos \alpha_i) + \sum_{i<j} u_2^{(T)}(|r_i - r_j|) \right) \right], \tag{3.1}
\]

with the molecule–\(^{4}\)He correlation \( u_1^{(T)} \) and the \(^{4}\)He–\(^{4}\)He correlation \( u_2^{(T)} \) given by

\[
u_1^{(T)}(r, \cos \alpha) = -(c/r)^5 \tag{3.2}
\]

\[
u_2^{(T)}(r) = -(b/r)^5 \tag{3.3}
\]

with \( c = 7.392 \text{ Å} \) and \( b = 2.670 \text{ Å} \). The precise form of the trial function is not important because we use descendant weighting for obtaining unbiased values for \( g(r, \cos \alpha) \). Such an isotropic trial function was found to be adequate for previous important sampled DMC calculations for HCN in small clusters [14]. This is expected from the weak anisotropy of the HCN-He interaction. Fig. 1 shows contours of the molecule-helium interaction potential \( V_X \) for HCN-\(^{4}\)He. For computational efficiency we introduce a cut-off for both the \(^{4}\)He–\(^{4}\)He interaction and its correlation \( u_2^{(T)} \) at a radius \( r_c = 8 \text{ Å} \), and replace \( u_2^{(T)} \) by a smooth function [59]

\[
\bar{u}_2^{(T)}(r) = u_2^{(T)}(r) - u_2^{(T)}(r_c) - (r - r_c) \left. \frac{du_2^{(T)}(r)}{dr} \right|_{r=r_c}. \tag{3.4}
\]

For completeness, we report the ground state energetics of HCN in bulk \(^{4}\)He obtained within these calculations. In order to correct the total potential energy for the error introduced by the cut-off, we assume a homogeneous \(^{4}\)He equilibrium density \( \rho \) at zero pressure, and approximate the missing contribution to the total ground state energy, \( E_{\text{corr}} = (\rho/2) \int_{r_c}^{\infty} d^3 r V_{\text{He}}(r) \). This is not a highly accurate correction, but the exact value of the ground state energy is immaterial for our calculation of \( g(r, \cos \alpha) \). For the equilibrium density \( \rho = 0.22 \text{ Å}^{-3} \), the DMC sampling yields an uncorrected ground state energy of \( E'/N = -7.35 \pm 0.006 \text{ K} \). The correction is \( E_{\text{corr}}/N = -0.95 \text{ K} \) per \(^{4}\)He atom. Thus we find a total energy of approximately \( E/N = -8.3 \text{ K} \) for both HCN and DCN. The chemical
potential of the molecule $\mu$ is the difference between the energy $E$ of molecule and helium and the energy of pure helium, $E_0 = N \times 7.2\text{K}$ at equilibrium. Hence we find $\mu \approx -282\text{K}$ for HCN and DCN in bulk $^4\text{He}$.

In Fig. 2, the pair distribution $g(r, \cos \alpha)$ (eq. (2.28)) is shown for HCN in bulk $^4\text{He}$, simulated by 256 $^4\text{He}$ atoms in a box of 23.0Å length on each side with periodic boundary conditions applied. For DCN, we used the same box size. The coordinates $r$ and $\alpha$ are the radial and polar spherical coordinates in the center of mass frame of the HCN molecule, with the molecular symmetry axis as the z axis.

Due to the small anisotropy of the $^4\text{He}$-HCN and $^4\text{He}$-DCN potential, and the large zero-point rotational motion of the molecule, the pair distribution $g(r, \cos \alpha)$ is only slightly anisotropic. In Fig. 3 we show the Legendre expansion coefficients $g_\ell(r)$ of $g(r, \cos \alpha)$, whose Bessel transform is the quantity entering the calculation of the self energy (2.34). In the limit of $B \to \infty$, the zero-point motion would completely delocalize the molecule orientation with respect to the surrounding $^4\text{He}$. In this situation, $g(r, \cos \alpha)$ would be isotropic, $g_{\ell>0}(r) = 0$, and therefore the self energy correction to $B_{\text{eff}}$ would vanish, $B_{\text{eff}} = B$. With the large but finite $B$ value of HCN, the Legendre expansion coefficients $g_{\ell>0}(r)$ are not negligible. As can be seen from Fig. 3, the quadrupole coefficient $g_2(r)$ is the main contribution to the anisotropy of $g(r, \cos \alpha)$ for HCN.

We recall that for the derivation of the rotational self energy expression (2.34), the uniform limit approximation was applied (see discussion in section 1A). For the Legendre expansion, this translates into the coordinate space approximations $g_{\ell=0}(r) \approx 1$ and $g_{\ell>0} \ll 1$. While all higher expansion coefficients $g_{\ell>0}(r)$ never exceed values of 0.2 in absolute value, $g_0(r)$ deviates from unity considerably, varying between 0 and values of almost 2. However, since, due to the selection rules, $\Sigma J(\omega)$ is independent of $g_{\ell=0}$, we see that the extent of angular modulations in the helium solvation density are consistent with the uniform limit and that this is therefore a good approximation for the purpose of calculating purely rotational excitations of a light rotor like HCN and DCN. We note that for the heavier linear rotor OCS, which has a stronger and more anisotropic interaction with helium [60], the angular modulation in the first layer of helium around OCS is considerably larger than [4] for HCN (Fig. 3). Hence the expansion coefficients $g_{\ell}(r)$ will be considerably larger and use of the uniform limit approximation would be more questionable for OCS.
IV. RESULTS: EXCITED STATES

A. Rotational Energies of HCN and DCN in $^4$He

The excitation energies are obtained as the solutions $\omega_J$ of eq. (2.33). Unlike for a linear molecule in the gas phase (where $\Sigma_J(\omega) = 0$), it is possible that more than one solution exists for a given $J$. In the next section, we will show that this is actually the case for $J = 2$ and $J = 3$ (and presumably for higher $J$'s). The existence of several solutions is not surprising considering that $\omega_J$ are the approximate excitation energies of a many-body system.

Table I lists the energies of the primary rotational excitation for $J = 1, 2, 3$. By “primary” we refer to the excitation of lowest energy, when we find more than one solutions of eq. (2.33). The occurrence of several lines for a given $J$ is discussed in the next section and in appendix A. Also shown in table I are the respective experimental excitation energies for HCN and DCN obtained by microwave spectroscopy [1]. Only the energy for $J = 1$ could be measured experimentally, because the helium cluster temperature of $T = 0.38$K is too low to allow appreciable population of rotationally excited states for this system.

B. Absorption Spectra of HCN in $^4$He

As discussed in more detail in section IV.E, the self energy $\Sigma_J(\omega)$ is complex, and the excitations obtained from eq. (2.33) are therefore not true eigenstates but decay as a result of the coupling to $^4$He excitation modes. This effect is observed in the molecule absorption spectrum $S_J(\omega)$, eq. (2.38), in the weak field $V^{(\text{ext})}$ of frequency $\omega$.

In a spectroscopic experiment, the frequency $\omega$ of a microwave laser field is scanned to obtain the rotational spectrum. Since the wavelength is much longer than the size of the molecule, only the dipole component of $V^{(\text{ext})}(\Omega)$, corresponding to the $J = 1$ component, is non-negligible. As a zero-temperature method, DMC/CBF only describes excitations from the ground state to an excited state. Hence, with the dipole field $V^{(\text{ext})}_{1M}$ acting on the molecule, we obtain only the $J = 0 \rightarrow 1$ rotational excitation(s). This corresponds to the $R(0)$ spectral line. Neither the $J = 1 \rightarrow 2, 2 \rightarrow 3, \ldots$ excitations corresponding to $R(1), R(2)$ and $R(3)$ spectral lines, nor the de-excitations $J = 1 \rightarrow 0, 2 \rightarrow 1, \ldots$ corresponding to the $P(1), P(2)$ spectral lines are obtained directly. However, one can go from the
ground state to \( J = 2, 3, \ldots \) simply by directly applying perturbations \( V_{J\mathcal{M}}^{(\text{ext})} \), \( J = 2, 3, \ldots \), i.e. via quadrupole-, octopole-, etc. transitions. Unlike in experiment, it is much easier in our CBF calculation to apply these multipole perturbations rather than formulate and solve the problem in a finite temperature theory. It has the added benefit that the zero-temperature absorption spectra \( S_J(\omega) \) resulting from application of dipole, quadrupole, etc., perturbations are simpler to interpret than finite temperature spectra, while still containing all the information about the energetics of the system. In Fig. 4 we plot the resulting absorption spectra \( S_J(\omega) \), \( J = 1, 2, 3 \), for HCN, where we have set both the field strength \( V_{J\mathcal{M}}^{(\text{ext})} \) and the dipole moment of HCN/DCN to unity (these factors will only scale the intensities of the spectra). The DCN spectra looks very similar. As we have pointed out above (section II A), we correct the energy denominator of the self energy in (2.37) by using the experimental phonon-roton spectrum instead of the Bijl-Feynman spectrum. However, we have not further replaced \( B\ell (\ell + 1) + \Re \Sigma(\omega) \) by \( \hbar \omega_{\ell} = B\ell (\ell + 1) + \Sigma(\omega) \). A detailed discussion about the effect of these and other phenomenological corrections can be found in appendix C.

Without \(^4\text{He} \) surrounding the molecule, we have \( \Sigma_J(\omega) = 0 \), i.e. the spectrum is a delta function centered at the free rotor energy

\[
S_J^{(\text{free})}(\omega) = \Im \left[ (\hbar \omega - BJ(J + 1) + i\varepsilon)^{-1} = \pi \delta (\hbar \omega - BJ(J + 1)) \right].
\] (4.1)

In Fig. 4 the free rotor lines are indicated by dashed vertical lines.

In the CBF approximation, the self energy \( \Sigma_J(\omega) \) is finite with both a real and an imaginary part. The associated absorption spectrum \( S_J(\omega) \) shows two kinds of features – sharp peaks and broader bands. We first analyze the sharp peaks. The origin of sharp peaks in \( S_J(\omega) \) are discussed in detail in appendix A We show there how an imaginary part that is small relative to \( B\ell (\ell + 1) + \Re \Sigma_J \) leads to a Lorentzian peaked at the energy \( \hbar \omega_J \), that is obtained as the solution (or one of the solutions) of \( \hbar \omega - BJ(J + 1) - \Re \Sigma_J(\omega) = 0 \). The energy \( \hbar \omega_J \) can be associated with a rotational excitation of finite life-time, which decays into a combination of a molecular \( \ell < J \) state and an excitation of the helium environment. The width of the Lorentzian is given by \( \Im \Sigma_J(\omega_J) \) (see section IV E).

In Fig. 4 the spectra \( S_J(\omega) \) show sharp peaks of increasing width and decreasing height with increasing \( J \). This indicates that the coupling of the HCN rotation to the phonon-roton spectrum of bulk \(^4\text{He} \) is stronger for higher energies. The lowest molecular mode \( J = 1 \) has the weakest coupling, evidenced by the fact that \( S_1(\omega) \) is very close to the spectrum of a free
rotor at $T = 0$, i.e. it has a single sharp line. In the next section we will obtain the effective rotational constant $B_{\text{eff}}$ from this line and compare with the corresponding experimental measurement. The exact width of the $J = 1$ spectral line is subject to computational uncertainties related to the DMC ground state calculation, as explained in section IV E and therefore cannot be directly compared with the experimental line width. In contrast to the single peak seen for $J = 1$, the spectra for $J = 2$ and $J = 3$ show several distinct sharp peaks. As explained in the appendix A, calculation of the position of a peak can result in several solutions. In some cases, the associated peaks have very small weight, but for $J = 2$ and $J = 3$, we find two clearly discernible peaks. Detailed analysis of the origin of these two peaks is also presented below in appendix A. The analysis shows that this two-peak structure of $S_J(\omega)$ is a direct consequence of the divergent density of states of $^4\text{He}$ at the roton minimum and the maxon maximum. Coupling to these divergences effectively splits the single free peak into two, and shifts one of the resulting peaks below the roton minimum and the other above the maxon maximum. Both peaks lie very close in energy to the divergent density of states of the phonon-roton dispersion. Therefore the motion of the molecule can couple to many excitations and the molecule rotates in a dense cloud of virtual roton and maxon excitations. Because of energy conservation, excitation of real rotons and maxons is not allowed at the energies of the two peaks. If it were allowed, it would lead to immediate damping of the rotation and we would not see well-defined peaks.

We consider now the origin of the broader bands of $S_J(\omega)$ in Fig. 4. These broader bands are seen as additional features in the spectra for $J = 2$ and $J = 3$, between the two peaks. This is more clearly seen in Fig. 5 where the absorption spectra are now plotted all on the same scale and are shown together with the density of states for the bulk+freely translating particle excitation spectrum $\varepsilon(p) + \hbar^2 p^2/2M$ (bottom panel). In the energy range $E = 12.0 - 15.1\text{K}$, $S_2$ has a high energy wing that is clearly aligned with the energy corresponding to maxon-roton excitations in $^4\text{He}$ plus a recoiling HCN molecule. This wing structure is thus a signature of efficient coupling of the molecule to high-energy excitations in $^4\text{He}$ that lie between the roton minimum and the maxon maximum. Excitations of the molecule in this wing feature are virtual, i.e. the molecule remains in its ground state $\ell = 0$. Another roton-maxon wing results from the coupling of the rotons and maxons with the $\ell = 1$ state of the molecule. Hence this wing is shifted by $B\ell(\ell + 1) = 2B$ and corresponds to the generation of a high-energy $^4\text{He}$ excitation together with translational recoil of the
molecule, plus a molecular rotational excitation \( \ell = 1 \), i.e. the molecule is now not only translated but is also excited rotationally to the \( \ell = 1 \) state. \( S_3 \) shows qualitatively the same features. In contrast, in \( S_1 \) the roton-maxon wings are negligibly small. The primary peak has almost all the strength of the spectrum, because the dipole field directly couples to the \( J = 1 \) excitation energy of the molecule, the energy of which is much lower than the roton. Thus, for \( J = 1 \) alone the absorption spectrum looks like a gas phase spectrum and can thus be described purely in terms of an effective rotational constant \( B_{\text{eff}} \) which determines the location of the single peak.

In principle there is an infinite series of roton-maxon wings for each \( \ell \), shifted by \( B\ell(\ell+1) \), with decreasing strength. However, with increasing energy \( \hbar \omega \), multi-phonon processes presumably become important. For example, in pure helium, these processes become important for energies above approximately 25 K, above which the dynamic structure function \( S(k, \omega) \) is dominated by multi-phonon excitations.\[61\] In our implementation of CBF theory, only one-phonon processes are taken into account.

Two technical details of our calculations are presented in the appendices. The first is the necessity to introduce a cut-off in the Legendre expansion of \( g(r, \cos \alpha) \) (appendix B). The second is a comparison of the effects of making the various phenomenological corrections to the self energy discussed in section II A (appendix C).

\section*{C. Effective rotational constant \( B_{\text{eff}} \) of HCN and DCN in \( ^4\text{He} \)}

From the position of the single peak in the absorption spectrum \( S_1 \) we can obtain the rotational excitation energy of the \( J = 1 \) excitation, \( \hbar \omega_1 \), from which we can obtain an effective rotational constant of \( B_{\text{eff}} \) assuming a free rotor spectrum:

\[ \hbar \omega_1 = 2B_{\text{eff}}. \]

This is the direct analog of the procedure used to obtain an experimental measurement of \( B_{\text{eff}} \) in Refs. 1, 2. Table IV compares the effective rotational constant of HCN and DCN, obtained from \( J = 1 \) only in this manner, with the corresponding measured values of Ref. 1. The statistical error of \( B_{\text{eff}} \) shown in the table is propagated from the DMC ground state calculation of \( g(r, \cos \alpha) \). The values of \( B_{\text{eff}} \) are in overall good agreement with the experimental values, agreeing to within 5\% for both molecules, although the error bars (\( \sim 2\% \))
are unfortunately too large to confirm the experimental determination of a slightly smaller ($\sim 1.5\%$) ratio $B_{\text{eff}}/B$ for the lighter HCN than for DCN. For both HCN and DCN, the calculated values of $B_{\text{eff}}$ are slightly larger than the experimental values. Such behavior of CBF theory to produce somewhat higher excitation energies than the corresponding experimental (exact) values has been observed in other cases \cite{32}. One remedy for this is to apply phenomenological correction to all terms in the energy denominator of $\Sigma_J(\omega)$ as we have explained above. The values given in table \text{[II]} were obtained by making such a correction only to the Bijl-Feynman spectrum for bulk helium, \textit{i.e.}, replacing this by the experimental collective excitation spectrum, but not modifying $B\ell(\ell + 1)$ or the free particle dispersion $\hbar^2 p^2/2M$. The additional effect of these further corrections is summarized in table \text{[III]} where we see a slight improvement of $B_{\text{eff}}$ in its agreement with the experimental values is obtained by making a self-consistent replacement of $B\ell(\ell + 1)$ by $\hbar \omega_\ell$. Further improvement could presumably be achieved by replacing the bare molecular mass $M$ by the effective mass $M_{\text{eff}}$ of HCN and DCN moving in $^4$He, if these quantities were known. However, we have checked that realistic changes in these quantities would not change the qualitative behavior of any of our results. These checks and relevant details for implementation of the phenomenological corrections are provided in appendix \text{[C]}.

Given that the value of $B_{\text{eff}}$ obtained here for HCN in bulk $^4$He is in good agreement with that measured in large droplets ($N > 1000$ helium atoms), it is interesting to compare also with the corresponding values calculated for small clusters \cite{14} (no experimental measurements have been made yet on small clusters). As noted in section \text{[II]} calculations of the $J = 1$ excitation by the POITSE methodology show that the resulting fitted value $B_{\text{eff}}$ does not converge to the large droplet value by $N = 25$, in contrast to the behavior of the heavier molecules such as OCS and SF$_6$. For these molecules, $B_{\text{eff}}$ converges to the corresponding droplet value before the first solvation shell is complete \cite{14, 17, 18, 20, 62, 63}. There are several possible reasons for this difference. First, our analysis for HCN in bulk $^4$He shows that a light rotating molecule leads to generation of collective excitations that are extended in space (phonons and rotons) instead of to formation of a local non-superfluid density in the first solvation shell that can adiabatically follow the molecular rotation \cite{14}. The cluster size dependence for these two different mechanisms might reasonably be expected to be very different, with the coupling to extended modes requiring more than a single solvation shell to approach its bulk character. A second possible explanation is that the projection operator
A used in Ref. 14 accesses a higher \( J = 1 \) state than the state associated with the rotation of the molecule, thereby causing the targeted excitation to overshoot not only the large droplet value but also the gas phase rotational energy. This effect was already seen in the POITSE excitation spectra of the smallest clusters calculated in Ref. 14, where multiple peaks were found, one of which was consistently above the gas phase rotational energy. For \( N = 1 \), comparison with the corresponding result obtained by the collocation method \[35\] confirmed that this excitation is indeed a higher lying \( J = 1 \) level. The POITSE method relies on having a good projection operator \( \hat{A}\Psi_0 \) which has sufficient overlap with the desired excited state. In this case one seeks a rotation of the molecule, but one that nevertheless involves considerable correlation of the molecule with the helium, as is evident from the second term in the CBF excitation operator, eq. (2.7). In contrast, the projector that has been used in both POITSE \[14, 17\] and related methods \[18\] to date is a free molecular rotor function, which corresponds only to the first term in eq. (2.7). This suggests that it will be worthwhile to use the full stationary CBF excitation operator \( \hat{A} = \delta U \) in a POITSE calculation, as we have already proposed in section II C above.

The situation seems to be opposite for heavier rotors in \(^4\text{He}\), namely here the direct approaches by evaluation and inversion of imaginary time correlation functions can provide a better description of the rotational dynamics. Thus, POITSE and related approaches are able to obtain accurate values for \( B_{\text{eff}} \) for OCS \[17, 18\], but our current implementation of CBF is not expected to be reliable in this case, as we have noted in section II A. We expect that working in the frame of the molecule would improve the CBF description to account also for the adiabatic following of \(^4\text{He}\) around such heavy rotors.

**D. Effective distortion constant \( D_{\text{eff}} \) of HCN and DCN in \(^4\text{He}\)**

We can use sharp spectral peaks for higher \( J \) values and fit to the spectroscopic energy levels for a non-rigid linear rotor, \( BJ(J + 1) - D(J(J + 1))^2 \) \[64\], where \( D \) is the centrifugal distortion constant. However, this fit should be used with considerable caution, for two reasons. First, as we have seen in section IV B, the deviations of the \( J = 0 \rightarrow 2 \) and \( 0 \rightarrow 3 \) transitions from an effective linear rotor are very large and have nothing to do with a true centrifugal distortion that might arise from a coupling of the molecular rotation to either a molecular or a localized helium vibration. In particular, these higher transitions
are split into two peaks which cannot both be fit by a simple phenomenological centrifugal distortion term. Second, both the statistical errors from the DMC and the errors stemming from the approximations used in CBF (see section II above) grow with \(J\), leading to larger overall errors associated with the peaks for higher \(J\) values. Nevertheless, by direct analogy again with the experimental procedure of fitting to spectral line positions, we can make a phenomenological fit to the \(J = 1\) spectral line together with the lowest spectral peak for each of the \(J = 2\) and \(J = 3\) spectra. The result is that because of the downward shift of the \(J = 2\) and \(J = 3\) lines induced by coupling to the roton-maxon excitations, we find a very large value of the fitted effective centrifugal distortion constant \(D_{\text{eff}}\). Thus, e.g., for HCN, while we obtain a value \(B_{\text{eff}} = \omega_1/2 = 1.266 \text{ cm}^{-1} (1.822 \text{ K})\) from the \(J = 1\) line only, fitting the \(J = 1\) and first \(J = 2\) peaks yields \(B_{\text{eff}} = 1.346 \text{ cm}^{-1} (1.937 \text{ K})\) and \(D_{\text{eff}} = 0.040 \text{ cm}^{-1} (0.058 \text{ K})\), and further fitting the \(J = 1\) and first \(J = 2\) and \(J = 3\) peaks all together yields \(B_{\text{eff}} = 1.320 \text{ cm}^{-1} (1.899 \text{ K})\) and \(D_{\text{eff}} = 0.035 \text{ cm}^{-1} (0.050 \text{ K})\). These values of \(D_{\text{eff}}\) are vastly enhanced over the gas phase value of the centrifugal distortion constant for HCN, \(D = 2.9 \times 10^{-6} \text{ cm}^{-1}\) \[65\], showing an increase of four orders of magnitude. Similar enhancements of several orders of magnitude have been observed in experimental fitted values of \(D_{\text{eff}}\) to multiple spectral lines for heavier molecules \[3\] and no theoretical explanation for these large enhancements has been given.

The fitting constant \(D_{\text{eff}}\) for HCN in helium and the gas phase centrifugal distortion constant \(D\) measure different physical effects. \(D\) is the usual measure of distortion of the linear rotor spectrum due to the non-rigid nature of HCN, which results in centrifugal forces acting on the component atoms as the molecule rotates, and hence in increased moments of inertia and lower rotational energy levels. \(D_{\text{eff}}\) is a measure of the deviation from the effective linear rotor spectrum caused instead, in the case of the weakly anisotropic HCN molecule, by the “back-flow” of the surrounding helium. As our CBF results clearly show, the “back-flow” effect on the energy spectrum is much bigger than centrifugal distortion of the bare molecule. Thus the observed enhancement factor with respect to the gas phase value, \(D_{\text{eff}}/D\), is not significant, and \(D\) can be neglected in the discussion of rotational spectra of molecules in helium.

In the first column of table IV we compare the effective distortion constant \(D_{\text{eff}}\) of HCN (from fitting to our CBF results) and OCS (fitted to experimental data) in helium. We also show values of \(D_{\text{eff}}\) obtained for HCN in a pseudo-hydrodynamic limit model, discussed in
section IV F. In the second and third column, we show the respective ratios $D_{\text{eff}}/B$ and $D_{\text{eff}}/B_{\text{eff}}$, i.e. we normalize $D_{\text{eff}}$ such that all (free) linear rotor spectra would collapse on the same curve $J(J+1)$.

We see from table IV that regardless whether we use either $D_{\text{eff}}$, or $D_{\text{eff}}/B$, or $D_{\text{eff}}/B_{\text{eff}}$ as a measure of distortion of the linear rotor spectrum, the HCN spectrum of excitation energies deviates considerably more from the linear rotor spectrum than does the spectrum of the heavier OCS molecule. We also see that the ratio $D_{\text{eff}}/B_{\text{eff}}$ is similar for OCS and HCN in the pseudo-hydrodynamic model. A possible explanation for this last observation is given in section IV F below.

The large value of $D_{\text{eff}}$ for HCN calculated here is a direct consequence of the high density of states in bulk helium near the roton-minimum and maxon-maximum, which are missing in the hydrodynamic limit model. This high density of states gives rise to a downward shift of the lower component of the split peaks for higher $J$ states, as discussed in section IV F above and explained in detail in appendix A. It also explains the greater distortion of the linear rotor spectrum compared to the distortion measured for OCS, since the considerably lower energy rotational excited states of OCS do not couple as effectively to the roton and maxon states as the rotational states of the lighter HCN molecule.

E. Rotation life-times and homogeneous linewidth

The self energy $\Sigma_J$ has a small, but finite imaginary part, which leads to a finite lifetime $\tau = 1/\Im m\Sigma_J$ of the rotational excitation, i.e. to homogeneous line broadening of the rotational absorption spectra. $\Im m\Sigma_J$ results from the principal value integration $\int dp$ in eq. (2.34) that is made when the energy denominator vanishes at some momentum $p = p_0$:

$$\Im m\Sigma_J = \frac{2B^2 \rho}{2J+1} \sum_{\ell} \frac{p_0^2}{S(p_0)} \frac{\sum_{\ell'} \tilde{L}(J,\ell',\ell)}{de(p_0)/dp + \hbar^2 p_0/M}, \quad (4.2)$$

with $p_0$ defined by

$$B\ell(\ell + 1) + \epsilon(p_0) = \hbar \omega. \quad (4.3)$$

The life-time is obtained by summing the contribution from all poles $p_0$. For calculation of the $J = 1$ excitation, Eq. (4.3) only has a solution for $\ell = 0$ and hence there is only one pole, because $\hbar \omega < B\ell(\ell + 1)$. From the selection rules (2.36), we find that $\ell' = 1$ and hence
we obtain the estimate of line width
\[
\Im \Sigma_{J=1} = \frac{2}{3} B^2 \rho \frac{p_0^3}{S(p_0)} \frac{\tilde{L}(1, 1, 0) g_2^2(p_0)}{d\varepsilon(p_0)/dp + \hbar^2 p_0/M}.
\] (4.4)

Unfortunately the value of the momentum at the poles for HCN and DCN is very small: 
\( p_0 = 0.19\AA^{-1} \) for HCN and \( p_0 = 0.15\AA^{-1} \) for DCN. These momentum values are too small for the corresponding Legendre component of the pair correlation function \( g_1(p_0) \) to be a reliable estimate. This can be seen by considering for simplicity the Fourier transform of a periodic function with period \( s \). The corresponding wave number \( p \) is discrete with smallest non-zero wave number equal to \( p_{\text{min}} = 2\pi/s \). In our case, \( s = 23.0\AA \) is the simulation box length. This results in a minimum wave number \( p_{\text{min}} = 0.27\AA^{-1} \), which is larger than the desired pole momentum values \( p_0 \) for HCN and DCN given above. Furthermore, we have the limiting value \( g_1(p) = O(p) \) for \( p \to 0 \). Hence the Legendre component at the pole \( g_1(p_0) \) is small, resulting also in a small value of \( \Im \Sigma_{J=1} \). This explains the small width of the \( J = 1 \) line evident in Figs. 4 and 5. However, since the statistical error of \( g_1(p) \) for small \( p \) is of the order of \( g_1(p) \) itself, we are not able to extract a reliable quantitative estimate of the \( J = 1 \) life-time and the associated linewidth.

\section*{F. Hydrodynamic Limit}

Hydrodynamical models have been used to describe rotations of heavy molecules with large moments of inertia solvated in \(^4\text{He} \). As we have noted already in the introduction, these models fail for light rotors like HCN when based on assumptions of adiabatic following. In this section we show that independently of any assumption of adiabatic following, any analysis of light rotor rotation involving hydrodynamic coupling to long wavelength helium modes cannot provide an adequate description of the coupled molecule-helium excitations dynamics because of the absence of coupling of rotational levels to \(^4\text{He} \) excitations of higher energy than the long wavelength phonon modes, \( i.e. \) to rotons and maxons.

We can simulate a hydrodynamic description of the \(^4\text{He} \) environment by replacing \( p \)-dependent \(^4\text{He} \) quantities by their low-\( p \) expansion:
\[
S(p) \to \frac{\hbar p}{2mc},
\]
(4.5)
\[
\varepsilon(p) \to \hbar cp.
\]
(4.6)
For simplicity, we keep the molecule-\(^4\)He pair distribution \(g(r, \cos \alpha)\) we have obtained from the quantum-mechanical DMC calculation. Therefore, our toy model is not a true hydrodynamical model, which would require calculation of \(g(r, \cos \alpha)\) for HCN solvated in a hydrodynamic environment. It should be noted that this “pseudo-hydrodynamic” model does not assume adiabatic following of the \(^4\)He \([4, 11]\). In the present context, “hydrodynamic” refers simply to the coupling to bulk helium modes with long wavelength.

In Fig. 6 we show the absorption spectra \(S_J, J = 1, 2, 3\) for HCN that are obtained with this pseudo-hydrodynamic model. These spectra show only sharp peaks and no broad bands, as expected from the discussion in section IV.B that assigned the broad bands to coupling to collective excitations in the maxon-roton region. Also, only a single spectral line is found for all three \(J\) levels. According to the analysis in section IV.B and in the appendix \([4, 11]\) (see also Fig. 8 in this appendix), this is also consistent with the lack of coupling to maxon-roton states. Fitting the positions of the three spectral peaks results in a good fit to a linear rotor spectrum, yielding effective spectroscopic constants \(B_{\text{eff}} = 1.376\text{cm}^{-1}\) (1.980 K) and \(D_{\text{eff}} = 0.00568\text{cm}^{-1}\) (0.00817 K), respectively, and a corresponding ratio value \(B_{\text{eff}}/B_0 = 0.931\). The reduction in rotational constant is significantly less than the experimentally observed reduction of 0.815, amounting to only \(\sim 36\%\) of the experimental reduction. This large discrepancy with the observed change of the rotational constant, in contrast to the good agreement achieved in section IV.C from coupling to the true helium excitation spectrum further confirms that the maxon-roton regime of excitations has a strong influence on the rotation of light rotors in \(^4\)He. It is therefore essential for a reliable model to either directly (as in the present CBF approach) or indirectly (e.g., as in the POITSE approach) allow for coupling of the rotational levels with those excitations.

The effective distortion constant \(D_{\text{eff}}\) is significantly reduced with respect to the full CBF result (see table IV), while its ratio \(D_{\text{eff}}/B_{\text{eff}}\) is similar to the corresponding ratio for OCS. This suggests that the effective distortion constant of OCS may be rationalized as resulting from coupling to long-wavelength phonons. Within the present CBF analysis, this is consistent with the observation that for OCS with a gas phase rotation constant \(B = 0.2029\text{cm}^{-1}\) (0.2920 K), the roton excitations are too high in energy to couple effectively to the molecular rotation. However, for OCS the local coupling to helium \([4, 11]\) needs also to be taken into account for a full analysis, as discussed in section \([4, 11]\) above. Consequently a consistent analysis of both \(B_{\text{eff}}\) and \(D_{\text{eff}}\) for OCS will most likely benefit from reformulating
the CBF theory in the molecular frame, as suggested in section II A.

Finally, it is interesting to note that this pseudo-hydrodynamic model severely underestimates the change of the rotational constant for HCN, as opposed to the over-estimation for HCN that was obtained from the previous hydrodynamic model of Ref. [7] that assumed complete adiabatic following of the molecular rotation by helium.

V. CONCLUSIONS

In this paper, we have derived the dynamic equations for molecular rotations in bulk $^4$He within the formalism of Correlated Basis Function (CBF) theory and applied them to HCN and DCN in superfluid bulk $^4$He at $T = 0$. For that purpose we have combined Diffusion Monte Carlo (DMC) calculations for the required ground state properties with the CBF theory for excitations. Energy levels, absorption spectra, and spectroscopic constants for rotational excitations of the HCN and DCN molecules were calculated from this combined theoretical approach which allows for coupling to collective $^4$He excitations. Our results for the effective rotational constants of HCN and DCN are seen to be in good agreement with the corresponding experimentally determined values [1]. The CBF values are slightly higher than the experimental results (by $\sim 5\%$ of $B$, corresponding to $\sim 25\%$ of the reduction $B - B_{\text{eff}}$), with about half of the difference being contained within the statistical error. We saw that the CBF values could be improved with systematic incorporation of more phenomenological input to the self energy. The statistical error derives from the DMC calculation of the molecule-helium correlation function and is hard to reduce further without imposing excessive computational requirements (the required sampling grows as the inverse square of the statistical error). For the present calculations with HCN and DCN, the statistical error of DMC is unfortunately too large to determine whether the experimentally observed small isotope effect ($\sim 1.5\%$) is correctly predicted by CBF.

An attractive feature of the CBF approach is the ability to calculate the full microwave absorption spectra at zero temperature. We calculated the spectra of the dipole, quadrupole, and octopole transitions of HCN, corresponding to $J = 0 \rightarrow 1$, $0 \rightarrow 2$, and $0 \rightarrow 3$. The $J = 0 \rightarrow 1$ transition is found to be very sharp and the dipole spectrum seen to have almost no features apart from the single Lorentzian peak centered at the $J = 1$ excitation energy. In contrast, the $J = 0 \rightarrow 2$ and $J = 0 \rightarrow 3$ transitions show weak phonon-maxon-
roton bands as well as secondary peaks. Both of these features are seen to be caused by the strong coupling of the molecule rotation to the roton and maxon excitations of $^4\text{He}$. This strong coupling was also seen to be responsible for the large values of the effective distortion constant $D_{\text{eff}}$ that result from fitting the primary peaks of the rotational excitation spectrum to the effective non-rigid linear rotor energy level expression $BJ(J+1) - D(J(J+1))^2$. The importance of the phonon-maxon-roton spectrum was further highlighted by a comparative calculation where the rotational excitations are calculated with coupling to a phonon dispersion mode alone (section IV F). In this pseudo-hydrodynamical model that lacks roton and maxon excitations, a much simpler absorption spectrum $S_J$ was found that possesses only a single peak for all $J$ values and no broad side-bands. The resulting empirically fit rotation constant is considerably higher than the experimental values, and smaller values of the effective distortion constant are seen. This shows that the coupling to the roton and maxon excitations of helium increases the deviation from the linear rotor spectrum. This coupling is strong for HCN and other light molecules, due to the vicinity of the $J = 2$ and $J = 3$ rotational levels to the roton energy.

A key feature of our CBF results is their demonstration that the coupling to phonons and rotons of the bulk helium environment accounts quantitatively for the observed reduction of the effective rotational constant $B_{\text{eff}}$ for HCN and DCN. For these light molecules, coupling to localized modes, e.g., as manifested by adiabatic following of some fraction of the first solvation shell helium density [4], can therefore be at most a very minor effect in the reduction of $B_{\text{eff}}$.

As far as methodology is concerned, the combination of DMC and CBF employed here facilitates the calculation of excitation energies in the CBF approximation because of the ease of implementing DMC, which provides the ground state pair distribution $g(r, \cos \alpha)$ needed for a CBF calculation. On the other hand, DMC is computationally much more expensive than the alternative of a full CBF calculation of both ground state and excitations. Even after extensive sampling, the statistical error of the $^4\text{He}$-HCN and $^4\text{He}$-DCN pair distribution function $g(r, \cos \alpha)$ was too large to be able to detect a statistically reliable difference between the rotational constants of the two isotopic species. Furthermore, with currently feasible simulation box sizes containing $N = 256$ $^4\text{He}$ atoms, we cannot reliably account for the long-range (small wave-length) correlations which are needed for the calculation of the homogeneous line width (section IV E). Ground state CBF, in contrast, is particularly reli-
able for long-range properties, while it yields only approximations to short-range properties, like the peak density of the first shell of $^4$He around the correlation hole of a $^4$He atom or a molecule. Thus, neither of these two approaches alone provides all the required ingredients to accurately obtain both the very small isotopic dependences of rotational constants and line widths for the HCN and DCN isotopomers.

In this work, we have considered the simplest implementation of the CBF analysis for molecular excitations in $^4$He, by assuming an infinite bulk $^4$He matrix. However, matrix isolation spectroscopy experiments are performed in droplets consisting of a few thousands of $^4$He atoms. As noted above, the inhomogeneous environment has been shown to possibly cause inhomogeneous line broadening and may be responsible for the $M$-splitting of the observed R(0) line for HCN. Another simplification made in the current CBF analysis was the disregard of coupling of rotation and translations of the molecule. This is justified at $T = 0$. At finite temperatures however, translational excitations will be populated, and these provide another source for inhomogeneous line broadening. The present CBF calculations can be generalized to molecules embedded in a finite quantum cluster which would allow quantification of the effect of a long range inhomogeneous helium environment (as distinct from the inhomogeneity in the local solvation shell around the molecule which is incorporated in this work) on the rotational dynamics of molecules. Finally we note that extension of the CBF approach presented here to heavy rotors like OCS and SF$_6$ may be feasible if the minimization of the action integral eq. (2.8) is performed in a frame rotating with the molecule, thus allowing also for coupling to $^4$He excitations localized around the molecule and for adiabatic following of some local $^4$He density.

Acknowledgments

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APPENDIX A: SELF-CONSISTENT SOLUTION OF EQ. (2.33)

The absorption spectra $S_J(\omega)$ of eq. (2.38) and (2.36) are complete descriptions of the spectrum in that they contain all the information about excitation energies that CBF theory can provide. However, it is instructive to take a closer look at precisely how the sharp peaks in $S_J(\omega)$ arise from eq. (2.38) and (2.36). The present discussion follows closely the discussion of appendix A in Ref. 26.

With the abbreviation

$$
\gamma_J(\omega) = BJ(J+1) + \Re \Sigma_J(\omega)
$$

we can write the spectrum as

$$
S_J(\omega) = \frac{\Im m \Sigma_J(\omega)}{(\gamma_J(\omega) - \hbar \omega)^2 + (\Im m \Sigma_J(\omega))^2}.
$$

Hence sharp peaks, i.e. long life-times of excitations of energy $\hbar \omega_0$, occur when $\gamma_J(\omega_0) = \hbar \omega_0$ and $\Im m \Sigma_J(\omega)$ is small. In this situation, $S_J(\omega)$ is small everywhere except near $\omega = \omega_0$.

In the vicinity of this region we can expand

$$
\gamma_J(\omega) - \hbar \omega = \alpha_J(\omega - \omega_0) \quad \text{with} \quad \alpha_J = \left[ \frac{d \Re \Sigma_J(\omega)}{d \omega} - 1 \right]_{\omega=\omega_0},
$$

and obtain a Lorentzian centered at $\omega_0$:

$$
S_J(\omega) = \frac{\epsilon_J}{\hbar^2 \alpha_J^2 (\omega - \omega_0)^2 + \epsilon_J^2}.
$$

Here we have assumed that $\Im m \Sigma_J(\omega)$ varies very little in the region close to $\omega_0$ and can consequently be replaced by $\epsilon_J = \Im m \Sigma_J(\omega_0)$. The weight of the peak is obtained by integration of the peak

$$
\int d\hbar \omega S_J(\omega) = \frac{\pi}{|\alpha_J|}.
$$

Hence we find the position of a peak by solving the equation

$$
\gamma_J(\omega) - \hbar \omega = 0
$$

for one or several roots $\omega_i$. We obtain the width of the peak from $\Im m \Sigma_J(\omega_i)$ and its weight from of $|d \gamma_J(\omega_i)/d \omega - 1|^{-1}$. All this applies only when $\Im m \Sigma_J(\omega_i)$ is small.

In Fig. 8 we show $\gamma_J(\omega) - \hbar \omega$ as function of $\hbar \omega$ for $J = 2$. In the range shown in the plots, $\gamma_J(\omega) - \hbar \omega$ has two roots, $\omega^{(1)}$ and $\omega^{(2)}$, indicated by black points. Since the imaginary part
of \( \Sigma_J(\omega^{(1)}) \) is small, \( S_J(\omega) \) has a sharp peak at \( \omega^{(1)} \), see Fig. 5. In contrast, \( \Im m \Sigma_J(\omega^{(2)}) \) is much larger, resulting in a broad peak at \( \omega^{(2)} \). Furthermore, both the real and imaginary part of \( \Sigma_J(\omega) \) vary significantly near \( \omega^{(2)} \), so that the peak is no longer Lorentzian. A broad band can be seen between the two peaks in Fig. 5. This broad band stems from the large values for \( \Im m \Sigma_J(\omega) \) when \( \hbar \omega \) lies in the roton-maxon band of the density of states, which is large between the two extremas of \( \varepsilon(p) + \hbar^2 p^2/2M \) (see lowest panel of Fig. 5).

It is easy to show that the density of states as well as \( \Im m \Sigma_J(\omega) \) diverges as the inverse square root of the energy at the extremas of \( \varepsilon(p) + \hbar^2 p^2/2M \) (see lower panel of Fig. 8). The real component \( \Re e \Sigma_J(\omega) \) also diverges as the inverse square root, but it does so on the “outer” sides of roton-maxon band (see upper panel of Fig. 8). These two divergences of \( \Re e \Sigma_J(\omega) \) and hence of \( \gamma_J(\omega) = \hbar \omega \) at the roton-maxon band are clearly responsible for the occurrence of two roots \( \omega^{(1)} \) and \( \omega^{(2)} \). In the pseudo-hydrodynamical model presented in section IV F we retain only the linear phonon dispersion and there is no roton-maxon band. Consequently, \( \Re e \Sigma_J(\omega) \) does not diverge anywhere and we find only a single peak for each \( J \) in the pseudo-hydrodynamic calculations.

APPENDIX B: \( \ell \)-CUT-OFF FOR \( g_\ell(p) \)

Since \( g(r, \cos \alpha) \), and therefore \( g_\ell(p) \), is affected by statistical noise, the self energy \( \Sigma_J(\omega) \) is also affected by this. For large \( \ell \), \( g_\ell(p) \) is small and the noise will exceed the true value of \( g_\ell(p) \). But \( \Sigma_J(\omega) \) is a functional of \( g_\ell^2(p) \), i.e. for large \( \ell \), the summation over \( \ell \) in eq. (2.34) adds only noise to \( \Sigma_J \) instead of converging. For that reason we introduce a cutoff \( \ell_{\text{cut}} \) to \( g_\ell(p) \), such that \( g_\ell(p) = 0 \) for \( \ell > \ell_{\text{cut}} \). In Fig. 7 we show the ratio \( B_{\text{eff}}/B_0 \) for HCN as a function of the cutoff \( \ell_{\text{cut}} \), where the phenomenological self energy with the experimental rather than the Bijl-Feynman excitation spectrum was used in the denominator. Fig. 7 shows clearly that for HCN the largest contribution to \( \Sigma_J(\omega) \) comes from \( \ell = 2 \), i.e. the quadrupole deviation from a spherical distribution around the molecule. Beyond \( \ell > 4 \), \( g_\ell(p) \) contributes very little to \( \Sigma_J \), therefore we choose \( \ell_{\text{cut}} = 6 \). The uncertainty associated with \( \ell_{\text{cut}} \) is much smaller than the statistical error of \( B_{\text{eff}}/B_0 \) that is propagated from the error of \( g(r, \cos \alpha) \).
APPENDIX C: CORRECTION TO $\Sigma_J(\omega)$

The self-energy $\Sigma_J(\omega)$ (2.34) was obtained by allowing for fluctuations of 2-body correlations and using the uniform limit approximation. As mentioned above, we can try to improve $\Sigma_J(\omega)$ without changing its analytic form, but instead by introducing a phenomenological energy denominator, obtained by i) using the experimental excitation spectrum instead of the Bijl-Feynman spectrum, ii) using the effective mass of HCN or DCN instead of the bare mass in $\hbar^2 p^2 / 2M$, or iii) using $\hbar \omega_{\ell}$ instead of $B\ell(\ell+1)$, as well as by combinations of these corrections.

For the last replacement, we have to solve eq. (2.33) self-consistently not only for $J = 1$, but simultaneously for all $J$, because of the occurrence of $\hbar \omega_{\ell}$ in $\Sigma_J$. Hence we solve the set of equations

$$\hbar \omega_J = BJ(J + 1) + \Re \Sigma_J(\omega_J), \quad J = 1, \ldots, J_{\text{max}}$$

with

$$\Sigma_J(\omega_J) = -B^2 \frac{(4\pi)^2 \rho}{2J + 1} \sum_\ell \int \frac{dp}{(2\pi)^3} \frac{p^2}{S(p)} \frac{\sum_{\ell'} \tilde{L}(J, \ell', \ell) g^2_{\ell'}(p)}{\hbar \omega_{\ell} + \epsilon(p) + \hbar^2 p^2 / 2M - \hbar \omega_J} \quad \text{(C2)}$$

We take the real part of the self energy, assuming that the imaginary part is small, since only then we have well-defined excitations, albeit decaying ones. We note that for $J > 1$, each one of eqns. (C1) has more than one solution, but we restrict ourselves to the solution which we believe corresponds to the effective rotational excitation of the molecule, i.e. to the main peak of $S_J$. This correspondence can only be established up to $J = 3$, hence we have to restrict ourselves to $J_{\text{max}} = 3$. For $J > 3$ we use $BJ(J + 1)$. In our view, solving eqns. (C1) for all other solutions as well and retaining the imaginary part of $\Sigma_J(\omega)$ would stretch the validity of a phenomenological correction of $\Sigma_J(\omega)$ and is therefore not warranted.

The resulting four combinations of different corrections of $\Sigma_J(\omega)$’s for HCN in bulk $^4$He are compared in table III. Clearly, the replacement of the Bijl-Feynman spectrum by the experimental excitation spectrum constitutes a significant correction of $\Sigma_J(\omega)$ and manages to reproduce the experimental values of $B_{\text{eff}}$. On the other hand, the self-consistent replacement of $B\ell(\ell + 1)$ by $\hbar \omega_{\ell}$ leads only to a minor further reduction of $B_{\text{eff}}$, almost within the statistical error of $\Sigma_J(\omega)$. Hence, we do not apply the latter correction in our calculations.

It is instructive to consider the effect of the molecular mass more carefully. Unfortunately, the effective mass $M_{\text{eff}}$ of HCN and DCN in $^4$He is unknown. CBF permits the calculation of effective masses but this would be beyond the scope of the paper. Therefore we used the bare
mass $M$ in the denominator of eq. (C2) for all our calculations. In principle, we can turn the argument around and compare the solution $\omega_J$ of eq. (C1) for $J = 1$ with the value for $\omega_1$ from the experiments of Ref. 1. However, on the level of CBF theory implemented in this paper, a precise prediction of the effective mass cannot be made, because $\omega_1$ depends only weakly on $M_{\text{eff}}$. In Fig. 9 we show the ratios of calculated versus experimental effective rotational constant, $B_{\text{eff}}/B_{\text{ex}}^{\text{eff}}$, for HCN and DCN as a function of the effective mass ratio $M_{\text{eff}}/M$, where $B_{\text{eff}} = 2\omega_1$ has been obtained from eqns. (C1) and (C2), using the experimental $^4\text{He}$ spectrum for $\epsilon(p)$. The error bars in Fig. 9 are estimated from the statistical error of $B_{\text{eff}}$ obtained from eqns. (2.33) and (2.34), with $M_{\text{eff}} = M$. The curves intersect $B_{\text{eff}}/B_{\text{ex}}^{\text{eff}} = 1$ at different values of $M_{\text{eff}}/M$, implying widely different effective masses for the two isotopes. However, the error bars are very large, and for most of the range in Fig. 9 the dependence of $B_{\text{eff}}$ on $M_{\text{eff}}$ is not statistically significant. Note also that we have neglected the effect of coupling of translation and rotation on $M_{\text{eff}}$. Coupling would of course introduce directional dependence of $M_{\text{eff}}$ in the molecular coordinate frame.
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Excitation energies of a Hermitian Hamiltonian are real. But we have eliminated the 2-body correlation fluctuations $\delta u_2(r_0, r_1, \Omega)$ from the equations of motion eqns. (2.15) and (2.17), and the resulting equation for $\delta u_1(r_0, \Omega)$ cannot be Hermitian anymore.
TABLE I: Energies of the primary rotational excitation of HCN and DCN. CBF denotes the present calculations employing CBF theory for excitations combined with exact ground state quantities calculated by DMC, and exp. refers to the experimental values of Ref. 1.

|       | HCN(CBF)       | HCN(exp.)       | DCN(CBF)       | DCN(exp.)       |
|-------|----------------|-----------------|----------------|-----------------|
| $J = 1$ | 2.53 cm$^{-1}$  | 2.407 cm$^{-1}$ | 2.08 cm$^{-1}$  | 1.998 cm$^{-1}$ |
| $J = 2$ | 6.64 cm$^{-1}$  | —               | 5.76 cm$^{-1}$  | —               |
| $J = 3$ | 10.8 cm$^{-1}$  | —               | 9.77 cm$^{-1}$  | —               |
TABLE II: Comparison of the calculated ratio $B_{\text{eff}}/B_0$ of HCN and DCN with the corresponding experimental values $^1$. CBF refers to the current CBF theory for excitations combined with exact ground state quantities calculated by DMC. Within the statistical error, the calculated ratios $B_{\text{eff}}/B_0$ for HCN and DCN cannot be distinguished from each other. The last column lists the corresponding moment of inertia increase (in uÅ$^2$) in CBF theory and in experiment, respectively.

|      | CBF       | experiment$^1$ | $\Delta I$ (CBF) | $\Delta I$ (exp.) |
|------|-----------|----------------|------------------|-------------------|
| HCN  | 0.857 ± 0.019 | 0.814          | 1.90 ± 0.29      | 2.61              |
| DCN  | 0.863 ± 0.016 | 0.830          | 2.22 ± 0.31      | 2.87              |
TABLE III: Comparison of the calculated ratio $B_{\text{eff}}/B_0$ for HCN obtained with and without the phenomenological corrections explained in the text. The four entries correspond to the four possible combinations of corrections in the energy denominator of the self energy $\Sigma_J(\omega)$: (i) the Bijl-Feynman spectrum (left column) or the experimental spectrum (right column), and (ii) the gas phase rotational energies (top row) or self-consistent solution of the rotational energies in helium, eqns. (C1) and (C2) (bottom row).

|                | Bijl-Feynman | exp. spectrum |
|----------------|--------------|--------------|
| $B\ell(\ell + 1)$ | 0.913        | 0.857        |
| $\hbar\omega_\ell$ | 0.910        | 0.841        |
TABLE IV: The effective distortion constant $D_{\text{eff}}$ and the ratios $D_{\text{eff}}/B$ and $D_{\text{eff}}/B_{\text{eff}}$ calculated for HCN in helium by the present combination of CBF and DMC, compared to the corresponding ratios derived from experimental measurements for OCS in helium droplets [66]. We also show the corresponding values calculated for HCN within the pseudo-hydrodynamical model of section IV F.

The last two columns give the gas phase reference values of the spectroscopic constants $B$ and $D$ for the two molecules.

|       | $D_{\text{eff}}$ (cm$^{-1}$) | $D_{\text{eff}}/B$ | $D_{\text{eff}}/B_{\text{eff}}$ | $B$ (cm$^{-1}$) | $D$ (cm$^{-1}$) |
|-------|-----------------------------|-------------------|-------------------------------|----------------|----------------|
| HCN   | 0.035                       | 0.0237            | 0.0265                        | 1.478 [65]     | 2.9×10$^{-6}$ [65] |
| OCS(exp. [66]) | 0.0004                   | 0.00197           | 0.00546                       | 0.0732         | 0.438×10$^{-7}$   |
| HCN(pseudo-hydro.) | 0.00568                   | 0.00384           | 0.00412                        |                |                |
FIG. 1: Contour plot of the HCN-$^4$He potential surface $V_X(R, z)$ from Ref. 34. Contour levels are shown at energy spacings of 5 K, with the outermost contour at -5 K, the next one at -10 K, etc. The linear HCN molecule is oriented along the $z$ axis such that the hydrogen points in the positive $z$ direction. $R$ is the cylindrical polar radius. At $z = 4.25 \text{Å}$ and $R = 0 \text{Å}$, the potential attains its minimum value of -42.4 K.
FIG. 2: Pair distribution $g(r, \cos \alpha)$ (eq. (2.28)), between HCN and $^4$He$_N$, for $N = 256$. $r$ is the distance between HCN and a $^4$He atom, and $\alpha$ is the angle between the directional vector from HCN to $^4$He and the HCN axis. The HCN-$^4$He interaction potential (see Fig. 1) is defined such that hydrogen is located on the positive side of molecule axis, i.e. at $\alpha = 0$. 
FIG. 3: Legendre expansion coefficients $g_\ell(r)$ of the pair distribution function $g(r, \cos \alpha)$, between HCN and $^4$He$_N$, for $N = 256$ in a cubic simulation box of length 23.0 Å.
FIG. 4: The absorption spectra $S_J(\omega)$, $J = 1, 2, 3$, for HCN in bulk $^4$He, where this is represented by $N = 256$ $^4$He in a box subject to periodic boundary conditions (see text). The dashed lines indicate the corresponding rotational excitation energies of HCN in the gas phase. The spectra have been broadened by a Lorentzian, by adding a small constant imaginary part of 10mK to the self energy $\Sigma_J(\omega)$. 
FIG. 5: The spectra $S_J(\omega)$, $J = 1, 2, 3$, for HCN in bulk $^4$He with all $S_J(\omega)$ now shown on same scale. For details of the representation of bulk $^4$He see Fig. 4 and text. The bottom panel shows in addition the dispersion curve $\varepsilon(p) + \hbar^2 p^2 / 2M$ and its density of states (“dos”) $[d\varepsilon(p)/dp + \hbar^2 p/M]^{-1}$. The vertical dashed and dotted lines indicate the onset of the roton-maxon band coupling with the $\ell = 0$ (dashed lines) and the $\ell = 1$ (dotted lines) rotational states of the molecule, respectively (see text).
FIG. 6: The absorption spectra $S_J(\omega)$, $J = 1, 2, 3$, for HCN obtained with the “pseudo-hydrodynamic model” in which the bulk $^4$He is replaced by a hydrodynamic model fluid having only long wavelength (phonon) modes, i.e., possessing linear dispersion. The simulation is made with $N = 256$ $^4$He in a box subject to periodic boundary condition and a length of 23.0Å. The dashed lines indicate the corresponding spectral positions for HCN in the gas phase.\cite{65}
FIG. 7: The effective rotational constant ratio $B_{\text{eff}}/B_0$ as a function of the cutoff $\ell_{\text{cut}}$ for HCN in bulk $^4$He, approximated by $N = 256$ $^4$He in a box subject to periodic boundary condition. We have truncated the Legendre expansion of the pair distribution $g(r, \alpha)$ at $\ell_{\text{cut}}$. The expansion has reached convergence at a value slightly higher than the experimentally measured ratio\cite{1} which is indicated by the horizontal line.
FIG. 8: Illustration of procedure for obtaining excitation energies from eq. (2.33). The upper panel shows $\gamma_J(\omega) - \bar{\hbar}\omega$ for $J = 2$, where $\gamma_J(\omega) \equiv B J(J+1) + \text{Re}\Sigma_J(\omega)$. The points emphasize the zeros of $\gamma_J(\omega) - \bar{\hbar}\omega$, which are the excitation energies for $J = 2$. For comparison, the dashed line shows $\gamma_J(\omega) - \bar{\hbar}\omega, J = 2, from our pseudo-hydrodynamic model, see section IV, where $\gamma_J(\omega) = \hbar\omega$ has only one solution, leading to the single peak shown in Fig. 6. The lower panel shows $\text{Im}\Sigma_J(\omega)$ for $J = 2$. Again, the dashed line indicates the corresponding result of the pseudo-hydrodynamic model. See text for a full discussion.
FIG. 9: The error of calculated versus experimental effective rotational constant, $B_{\text{eff}}/B_{\text{eff}}^\text{ex}$, for HCN and DCN as a function of the effective mass ratio $M_{\text{eff}}/M$. That the intersections of the curves with $B_{\text{eff}}/B_{\text{eff}}^\text{ex} = 1$ occurs at the same values of $M_{\text{eff}}/M$, is clearly not statistically significant because of the large error bars. The value of $B_{\text{eff}}^\text{ex}$ is taken from Ref. [1]. See appendix C for a discussion of the phenomenological corrections used in this figure.