Triatomic Molecular Systems and Three-body forces: The Ar₃ case

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Abstract. We performed bound state calculations to obtain the first few vibrational states for the Ar₃ molecular system. The equations used are of Faddeev-type and are solved directly as three-dimensional equations in configuration space, i.e. without resorting to an explicit partial wave decomposition. In addition to realistic pairwise interactions, we employ long range three-body forces. Our results are in good agreement with those obtained by other methods based on partial wave expansion and show a significant contribution of the three-body forces (>10%) to the binding energy and thus their inclusion is, in general, warranted in studying similar triatomic systems.

INTRODUCTION

In calculations of the vibrational spectra of triatomic inert gases, pairwise interactions are used as a first approximation. Three-body interactions are usually neglected on the assumption that their contribution is small, or on the ground that they are poorly known. For example, in the case of ⁴He trimer the contribution of the three-body forces to the binding is known to be small – of the order of < 1% [1]. In the case of Ar₃ system, however, it has been shown that the inclusion of three-body forces substantially improves the agreement between the third virial coefficient and experiment [2]. In view of the fact that realistic two-body forces and rigorous theoretical approaches are nowadays available, a systematic investigation of the role of three-body forces in trimers is warranted.

In the present work we are concerned with the calculation of the vibrational spectrum of the Ar₃ with and without three-body forces. The choice of this system is ideal for the following reasons: First, realistic inter-atomic forces are available [3] and therefore the role of three-body forces can be investigated unambiguously; second, unlike nuclear three-body systems, Ar₃ is a bosonic one and thus complications due to spin and isospin are absent. Therefore, effects form numerical inaccuracies can be minimized. Furthermore, the Ar₃ is known to exhibit the so-called “liquid-like” behavior making it a good candidate for investigating other phenomena such as recombination processes at ultra-low energies, low-temperature crystallization, photochemistry, etc. Moreover, the behavior of this trimer under certain external thermodynamical conditions especially those close to phase transitions are of extreme importance in understanding the influence of three-body forces on the gas-liquid coexistence of Argon.

In our investigations we employ three-body Faddeev-type equations in configuration...
space obtained within the framework of the total-angular-momentum representation [4]. These equations are solved as three-dimensional equations, i.e. without resorting to explicit partial wave decomposition and thus the question on whether enough partial waves are included or not is avoided.

OUR APPROACH

In the presence of both two- and three-body forces, the three-particle Hamiltonian reads [4]

\[ H_{3B} = H_0 + \sum_{i=1}^{3} V_i^{(2B)} + V^{(3B)} \]  

leading to a set of coupled differential Faddeev-type equations \((\hbar^2/2\mu = 1)\)

\[
\left[ H_0 + V_i^{(2B)}(x_i) + V^{(3B)}(x_i, y_i) - E_{3B} \right] \Phi_i(x_i, y_i) = -V_i^{(2B)}(x_i) \sum_{j \neq i} \Phi_j(x_j, y_j),
\]

where \(H_0\) is the free Hamiltonian, \(V_i^{(2B)}\) and \(V^{(3B)}\) are the two- and three-body potentials respectively, \(E_{3B}\) the binding energy, \((x_i, y_i)\) the Jacobi coordinates, and \(\Phi_i (i = 1, 2, 3)\) the Faddeev components. In the case of zero total angular momentum, and for identical particles, \(H_0\) is given by

\[ H_0 = -\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} - \left( \frac{1}{x^2} + \frac{1}{y^2} \right) \frac{\partial}{\partial z} (1 - z^2) \frac{\partial}{\partial z} \]  

where \(x = |x|\) is the usual two-body Jacobi coordinate, \(y = |y|\) the 2+1 coordinate, and \(z = \cos(x \cdot y)\). In order to obtain a solution, the energy \(E\) is treated as a parameter and thus Eq. (2) is transformed into an eigenvalue equation

\[ (EI - H_0 - \mathcal{V})^{-1}P\Phi = \Lambda\Phi \]  

where \(P\) is the total permutation operator of the coordinate variables, and \(\mathcal{V}\) contains all potential terms (details on the formalism can be found in Ref. [4]). We solve the three-dimensional Eq. (4) iteratively using the Arnoldi-type method. Physical solutions correspond to the cases when the eigenvalue \(\Lambda = 1\). Thus the problem of calculating the vibrational binding energies is reduced to finding the discrete spectrum of the operator

\[ \mathcal{L} = (EI - H_0 - \mathcal{V})^{-1}P. \]  

RESULTS AND DISCUSSION

We calculated the binding energies for the ground state and first excited state of the Ar₃ trimer by employing two variant highly repulsive Ar-Ar realistic potentials of Aziz [3]. For the three-body force we use the triple-dipole Axilrod-Teller type [5] interaction. The
results obtained using pairwise forces (2BF) and a combination of two- and three-body forces (2BF + 3BF) are shown in Table 1. It is seen that the results with both two- and three-body interactions are in fair agreement with, for example, those of Refs. [6] and [7], via different formalisms. It is clear that the Faddeev-type formalism employed is suitable in studies concerning three-molecular systems and the question of handling the multitude of couple equations for the various partial waves can be avoided by solving the three-dimensional equations directly. Such an approach is highly desirable when strong repulsive two-body forces are involved. The practically hard repulsive core nature of the inter-molecular van der Waals forces gives rise to strong correlations which require a large number of partial waves to obtain converged results. Finally, we mention that our results show a significant contribution to the binding from three-body forces (>10%). In this regard the inclusion of three-body calculations in triatomic molecular systems is, in general, warranted. Further compilation of results are underway.

| Potential | This work | Other works |
|-----------|-----------|-------------|
|           | 2BF       | 2BF + 3BF   | Ref. [6] | Ref. [7] |
| HFD-B2    | -0.0329   | -0.0356     | -0.0314 |
|           | -0.0297   | -0.0301     | -0.0286 |
| HFD-C     | -0.0327   | -0.0363     | -0.0316 |
|           | -0.0295   | -0.0325     | -0.0278 |

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