

Comment on “Optimization of Ground- and Excited-State Wave Functions and van der Waals Clusters”

In a recent Letter Nightingale and Melik-Alaverdian [1] used the correlation function quantum Monte Carlo method (CFMC) [2,3] to compute vibrational energy levels of Ar_n with n up to 7. In this Comment we point out that the trial functions used in Ref. [1] prevent the authors from obtaining odd-parity states and thus that they miss some of the levels.

The CFMC method uses a Monte Carlo imaginary-time projection method to obtain a very compact basis [2,3]. The Monte Carlo imaginary-time projector removes wave functions with larger energies from a starting basis of optimized many-parameter trial functions. Overlap and Hamiltonian matrix elements are computed in the final Monte Carlo projected basis and a small generalized eigenvalue problem is solved. The trial functions used by Nightingale and Melik-Alaverdian depend only on the interatomic distances which are all invariant under the inversion operation: none of their basis functions have odd parity. All of the physically allowed states of Ar_n are invariant under permutation of Ar nuclei, but not all allowed states have even parity. Clusters with more than three atoms will have odd-parity vibrational states.

We have used the polar coordinates associated with the diatom-diatom Jacobi vectors, a large basis, and the Lanczos algorithm to compute vibrational levels of Ar_4 . The potential is the same as that used in Ref. [1]. The basis functions we use are products of parity-adapted bend and stretch functions. The parity-adapted bend functions are products of associated Legendre functions and sine or cosine functions [4]. The stretch functions are products of three potential optimized discrete variable representation [5,6] functions.

We compute all eigenfunctions of the Hamiltonian operator and then select those that are invariant with respect to permutation of the Ar nuclei. This is done using a correlation table. The molecular symmetry group of Ar_4 is the permutation-inversion group $G_{48} = \{E, E^*\} \otimes S_4$, where $\{E, E^*\}$ is the inversion group and S_4 is the permutation group of four identical particles [7]. The coordinate symmetry group, $G_{16} = \{E, E^*\} \otimes G_8$, where $G_8 = \{E, (12)\} \otimes \{E, (34)\} \otimes \{E, (13)(24)\}$, is a group whose symmetry we can exploit easily. We label levels computed using the coordinate symmetry group with irreducible representations of the full symmetry group by using a correlation table.

We can compare the even-parity levels with those obtained by Nightingale *et al.* using the CFMC method. More accurate CFMC levels were published in Ref. [8]. See Table I. They agree well with our results. For every even-parity level there is an odd-parity level whose energy differs by less than 0.0001, indicating that there is little

TABLE I. A comparison of bosonic levels of this work and those computed with the CFMC method [1,8]. +/− refer to the even/odd parity.

Parity	Ref. [1]	Ref. [8]	This work
+	−5.118 11	−5.118 146 05	−5.1181
+	−4.785	−4.800 897 73	−4.8008
+	−4.674	−4.725 156 7	−4.7250
+	−4.530	−4.630 025	−4.6299
+	−4.39	−4.586 389	−4.5861
−			−4.5682
+			−4.5278
+			−4.4834
+			−4.4631
−			−4.4380
+			−4.4279

tunneling. There are odd-parity levels that are invariant under permutation of Ar nuclei (with even-parity partners that are not invariant under permutation of Ar nuclei). These cannot be computed with the trial functions of Ref. [1] because they depend only on interatomic distances. Using trial functions that are functions of only interatomic distances will prevent one from computing odd-parity vibrational states, which exist for any molecule with more than three atoms.

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