

Intermolecular Hamiltonian for solute–solvent_n clusters and application to the (1|1) isomer of anthracene–He₂

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Intermolecular kinetic-energy operators are derived (in the rigid monomer approximation) for solute–solvent_n clusters of the type B–A_n, where B is a molecule and A is either an atom or a molecule. The operators are obtained for a body-fixed frame embedded in the B moiety and parallel to the principal axes of that species. They are expressed in terms of intermolecular coordinates that represent the projection along the body-fixed axes of position vectors pointing from the center of mass of B to the centers of mass of the A species. The results are particularly useful for calculations on clusters in which A–B interactions dominate over A–A interactions in the intermolecular potential energy surface and/or there is minimal interaction between subsets of the A moieties. This utility is demonstrated in variational calculations of intermolecular states in the (1|1) isomer of anthracene–He₂. © 2003 American Institute of Physics. [DOI: 10.1063/1.1599831]

I. INTRODUCTION

A large body of work exists pertaining to the elucidation of the properties of clusters composed of a molecule (“B”) microsolvated by atoms or small molecules (“A”).¹ Such studies are valuable for the information that they can provide on intermolecular forces, solvent structure and dynamics, photodissociation dynamics, and finite-size effects on chemical processes, on electronic and nuclear excitations, and on order-disorder phase transitions, to name but several areas of interest. This literature is rich in both experimental (primarily spectroscopic) and theoretical/computational studies. Indeed, the nature of the species as rather weakly interacting many-body systems in which large-amplitude nuclear motions are prevalent often demands close coupling between experiment and simulation for significant progress to be made. In this regard, the simulation of nuclear dynamics arising from intermolecular motions within the cluster can be particularly valuable in shedding light on cluster properties. Such simulations have been performed by classical,² semiclassical,^{3,4} and quantal (e.g., Refs. 5–18) methods. However, most dynamically exact quantal simulations directly germane to characterization of intermolecular level structures have been limited to one-to-one complexes of the type B–A (e.g., Refs. 5–9, 11, 12, 15, though see Refs. 10 and 13 for examples of such calculations for $n > 1$). In large part this size limitation has been imposed by the lack of necessary computing power. With such power continuing to increase steadily, though, studies of larger systems are becoming much more feasible.

Our aim in this work is to help facilitate the application of dynamically exact (within the rigid-monomer approximation) intermolecular level-structure calculations to B–A_n species with $n \geq 2$. Our first main focus is on the intermolecular kinetic-energy operator for such species when A is an

atom. In particular, we derive that operator in terms of the $3n$ intermolecular coordinates that are the components of the position vectors from the center of mass of B to each of the A moieties, such components being measured with respect to a body-fixed (BF) axis system embedded in B. Thereby, we obtain for arbitrary n the kinetic-energy operator in terms of coordinates that are particularly useful when A–B interactions dominate over A–A interactions.

A second focus of the present work pertains to the intermolecular kinetic-energy operator of B–A_n clusters when A is a molecule. Specifically, we show that a generalization of the A=atom kinetic-energy operator to the A=molecule case is straightforward. Again, the resulting operator depends on coordinates that one would expect to facilitate the solution of the intermolecular problem when A–B interactions dominate over A–A ones.

Finally, in specific application of the above-mentioned results for A=atom we report calculations of the low-energy intermolecular level-structure of the (1|1) isomer of the anthracene–He₂ cluster (the isomer in which the He atoms are bound to opposite sides of the anthracene plane). Our interest in the species is threefold. First, it is relevant to spectroscopic results obtained on anthracene–He_n cluster beams.¹⁹ And, our results complement calculations reported elsewhere¹⁴ on the (2|0) (same-sided) isomer of the cluster. Second, the (1|1) isomer is a good example of the significant effect that kinetic-energy coupling terms can have on the intermolecular states of B–A_n clusters. Notably, such terms are neglected under the approximation that the B moiety is fixed in space (infinitely massive). Last, the species is an excellent model case illustrating how the cost of intermolecular level-structure calculations on B–A_n species can be reduced significantly with little loss of accuracy in situations where some or all A–A pairwise interactions are small.

The paper is organized as follows. In Sec. II we derive the intermolecular vibrational ($J=0$) kinetic-energy operator for B–A_n, where A is an atom. Section III pertains to the

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analogous derivation for the case where A is a molecule. In Section IV we outline the procedure employed for the calculation of the intermolecular states of the (1|1) isomer of anthracene-He₂ and of the anthracene-He complex. Section V then presents the results of the intermolecular calculations. A main focus of this section is on the great utility of considering the (1|1) states in terms of zeroth-order states constructed from products of anthracene-He eigenstates. Section VI concludes.

II. KINETIC-ENERGY OPERATOR FOR B-A_n CLUSTERS WHEN A IS AN ATOM

We consider a cluster of the form B-A_n where B is a molecule and A is an atom. To obtain the intermolecular kinetic-energy operator for the species we proceed by obtaining a classical expression for that energy and then convert that to a quantal operator by using the Podolsky transformation.²⁰ The classical kinetic energy, T , of such a species minus that associated with translation of its center of mass is given by²¹

$$2T = m_B \dot{\mathbf{r}}_B^2 + m_A \sum_{i=1}^n \dot{\mathbf{r}}_i^2 + \sum_{\alpha} \frac{1}{I_{\alpha}} j_{\alpha}^2, \quad (1)$$

where the labels $i = 1 \dots n$ refer to the A moieties, m_A and m_B are the masses of A and B, respectively, the \mathbf{r}_i are the position vectors of the A species with respect to the center of mass of the cluster, \mathbf{r}_B is the position vector of B's center of mass with respect to that of the cluster, the dots (here and below) denote time differentiation of vector components measured with respect to a space-fixed axis system with origin at the cluster center of mass, the index α runs over the three principal axis directions of B, the j_{α} are the components of the angular momentum of B about its center of mass measured with respect to its principal-axis system, and the I_{α} are the principal moments of inertia of B. Defining T' such that

$$2T' \equiv m_B \dot{\mathbf{r}}_B^2 + m_A \sum_{i=1}^n \dot{\mathbf{r}}_i^2 \quad (2)$$

and the internal coordinates

$$\mathbf{d}_i \equiv \mathbf{r}_i - \mathbf{r}_B; \quad i = 1, 2, \dots, n, \quad (3)$$

which represent the vectors from the center of mass of B to each of the A moieties, it is straightforward to show that

$$2T' = m_A \left(\sum_{i=1}^n \dot{\mathbf{d}}_i^2 \right) - \frac{m_A^2}{M} \left(\sum_{i=1}^n \dot{\mathbf{d}}_i \right)^2. \quad (4)$$

The momenta conjugate to the \mathbf{d}_i (denoted \mathbf{p}_i) can be obtained by taking derivatives of T with respect to the $\dot{\mathbf{d}}_i$.²¹ Since the j_{α} and I_{α} are independent of the $\dot{\mathbf{d}}_i$, this is equivalent to finding the analogous derivatives of T' . From Eq. (4) one finds

$$\mathbf{p}_i = m_A \dot{\mathbf{d}}_i - \frac{m_A^2}{M} \sum_{k=1}^n \dot{\mathbf{d}}_k. \quad (5)$$

With Eq. (5) and a little algebra Eq. (4) becomes

$$T' = \frac{1}{2\mu} \sum_{i=1}^n \mathbf{p}_i^2 + \frac{1}{m_B} \sum_{k>i=1}^n \mathbf{p}_i \cdot \mathbf{p}_k, \quad (6)$$

where $\mu \equiv m_A m_B / (m_A + m_B)$. Finally,

$$T = \frac{1}{2\mu} \sum_{i=1}^n \mathbf{p}_i^2 + \frac{1}{m_B} \sum_{k>i=1}^n \mathbf{p}_i \cdot \mathbf{p}_k + \sum_{\alpha} \frac{1}{2I_{\alpha}} j_{\alpha}^2. \quad (7)$$

Equation (7) is converted into a quantal operator by a trivial Podolsky transformation,²⁰ yielding

$$\hat{T} = \frac{1}{2\mu} \sum_{i=1}^n \hat{\mathbf{p}}_i^2 + \frac{1}{m_B} \sum_{k>i=1}^n \hat{\mathbf{p}}_i \cdot \hat{\mathbf{p}}_k + \sum_{\alpha} \frac{\hat{j}_{\alpha}^2}{2I_{\alpha}}, \quad (8)$$

where

$$\hat{\mathbf{p}}_i \equiv -i \left(\frac{\partial}{\partial X_i}, \frac{\partial}{\partial Y_i}, \frac{\partial}{\partial Z_i} \right)$$

and (X_i, Y_i, Z_i) are the Cartesian components of \mathbf{d}_i measured with respect to a space-fixed axis system. Equation (8) as it stands is not particularly useful since expression of the potential energy of the cluster in terms of the space-fixed components of the \mathbf{d}_i is very inconvenient. Therefore, we re-express \hat{T} in terms of BF components of the $\mathbf{d}_i \equiv (x_i, y_i, z_i)$. As BF frame we choose an axis system centered at the center of mass of the cluster with axes parallel to the principal axes of B. In terms of these coordinates Eq. (8) becomes

$$\hat{T} = -\frac{1}{2\mu} \sum_{i=1}^n \nabla_i^2 - \frac{1}{m_B} \sum_{k>i}^n \nabla_i \cdot \nabla_k + \sum_{\alpha} \frac{\hat{j}_{\alpha}^2}{2I_{\alpha}}, \quad (9)$$

where

$$\nabla_{\alpha} \equiv \left(\frac{\partial}{\partial x_i}, \frac{\partial}{\partial y_i}, \frac{\partial}{\partial z_i} \right)$$

and where we have made use of the rotational invariance of ∇_i^2 and $\nabla_i \cdot \nabla_k$.

We have one remaining issue to address in \hat{T} , as given by Eq. (9). That is, we seek expressions for the \hat{j}_{α} , the operators corresponding to the rotational angular momentum of B about its center of mass, as measured along the BF axes. We start by noting that

$$\hat{j}_{\alpha} = \hat{J}_{\alpha} - \hat{l}_{\alpha}, \quad (10)$$

where \hat{J}_{α} is the operator corresponding to the total angular momentum of the cluster measured along the α th principal axis of B, and \hat{l}_{α} is the operator corresponding to the total orbital angular momenta of the n atoms and B about the cluster center of mass measured along the α th principal axis of B. We can find the \hat{l}_{α} by starting with the classical orbital angular momentum vector

$$\mathbf{l} = m_B \mathbf{r}_B \times \dot{\mathbf{r}}_B + m_A \sum_{i=1}^n \mathbf{r}_i \times \dot{\mathbf{r}}_i, \quad (11)$$

where, again, the dot denotes time differentiation of vector components measured along the space-fixed axes. By inverting Eq. (3) and using Eq. (5), one can show that

$$\mathbf{l} = \sum_{i=1}^n \mathbf{d}_i \times \mathbf{p}_i. \quad (12)$$

Given Eq. (12), the expression for the space-fixed components of $\hat{\mathbf{l}}$ in terms of the (X_i, Y_i, Z_i) is easily found to be

$$\hat{\mathbf{l}}^{\text{SF}} = \sum_{i=1}^n \mathbf{d}_i \times \hat{\mathbf{p}}_i \equiv \sum_{i=1}^n \hat{\mathbf{l}}_i^{\text{SF}}, \quad (13)$$

where

$$\hat{\mathbf{l}}_i^{\text{SF}} = -i(X_i, Y_i, Z_i) \times \left(\frac{\partial}{\partial X_i}, \frac{\partial}{\partial Y_i}, \frac{\partial}{\partial Z_i} \right). \quad (14)$$

It is straightforward to show¹² starting from Eq. (14) that the BF components (i.e., components along the principal axes of B) of the $\hat{\mathbf{l}}_i$ are given by

$$\hat{\mathbf{l}}_i^{\text{BF}} = -i(x_i, y_i, z_i) \times \left(\frac{\partial}{\partial x_i}, \frac{\partial}{\partial y_i}, \frac{\partial}{\partial z_i} \right). \quad (15)$$

Summing over i and using Eq. (10), Eq. (9) becomes

$$\hat{T} = -\frac{1}{2\mu} \sum_{i=1}^n \nabla_i^2 - \frac{1}{m_B} \sum_{k>i=1}^n \nabla_i \cdot \nabla_k + \sum_{\alpha} \frac{(\hat{J}_{\alpha} - \sum_i \hat{l}_{i,\alpha})^2}{2I_{\alpha}}, \quad (16)$$

with the $\hat{l}_{i,\alpha}$ given by Eq. (15) (the superscript ‘‘BF’’ being dropped for clarity). Finally, we separate \hat{T} into a rotationless ($J=0$) part and a rotation–vibration ($J \neq 0$) part

$$\hat{T} = \hat{T}_v + \hat{T}_{rv}, \quad (17a)$$

where

$$\hat{T}_v \equiv \sum_{i=1}^n \left[-\frac{\nabla_i^2}{2\mu} + \sum_{\alpha} \frac{\hat{l}_{i,\alpha}^2}{2I_{\alpha}} \right] + \sum_{k>i=1}^n \left[-\frac{\nabla_i \cdot \nabla_k}{m_B} + \sum_{\alpha} \frac{l_{i,\alpha} l_{k,\alpha}}{I_{\alpha}} \right] \quad (17b)$$

and

$$\hat{T}_{rv} \equiv \sum_{\alpha} \frac{(\hat{J}_{\alpha}^2 - 2\hat{J}_{\alpha} \sum_{i=1}^n \hat{l}_{i,\alpha})}{2I_{\alpha}}. \quad (17c)$$

To obtain Eq. (17c) we have used the fact that all components of $\hat{\mathbf{J}}$ commute with all the $\hat{l}_{i,\alpha}$. This is a direct result of $\hat{\mathbf{J}}$ being the generator of rotations of the whole cluster,⁸ the BF components of the \mathbf{d}_i are unaffected by $\hat{\mathbf{J}}$.

Equation (17b) is one of the main results of this paper. It is pertinent to examine it in some detail. First, one notes that the case of a cluster in which the B moiety is fixed in space is recovered in the limit where m_B and the I_{α} approach infinity, in which case

$$\hat{T}_v = -\sum_{i=1}^n \frac{\nabla_i^2}{2m_A}. \quad (18)$$

Comparison of Eq. (18) and Eq. (17b) indicates that the assumption of a rigidly fixed B moiety can introduce signifi-

cant error into a level-structure calculation and that the magnitude of that error will increase with m_A/m_B . Second, when $n=1$ Eq. (17b) becomes

$$\hat{T}_v \equiv -\frac{\nabla_1^2}{2\mu} + \sum_{\alpha} \frac{\hat{l}_{1,\alpha}^2}{2I_{\alpha}}, \quad (19)$$

which is identical to the kinetic-energy operator that has been used extensively in level-structure calculations of aromatic-rare gas complexes.^{6,8,9} In the light of Eq. (19), it is clear that \hat{T}_v of Eq. (17b) consists of two types of terms. One, corresponding to the first summation on the right hand side (rhs) of the equation, is a sum of kinetic-energy operators, each identical to that for a single atom interacting with B. The other term, corresponding to the second summation on the rhs of the equation, constitutes pairwise kinetic couplings between atoms that arise due to the translation and rotation of B.

Finally, and most important, it is useful to examine the implications of Eq. (17b) in cases where there are two (or more) groups of A atoms distinguished by lack of appreciable A–A interactions between atoms of the different groups. For example, consider the case of a rare-gas-solvated aromatic in which m atoms are localized on one side of the aromatic, $n-m$ atoms are localized on the opposite side, and there is no appreciable pairwise interaction between the atoms of these two types. The intermolecular potential energy function can then be written as

$$V(\mathbf{d}_1 \dots \mathbf{d}_n) = v^{(m)}(\mathbf{d}_1 \dots \mathbf{d}_m) + v^{(n-m)}(\mathbf{d}_{m+1} \dots \mathbf{d}_n), \quad (20)$$

and the full $J=0$ intermolecular Hamiltonian can be expressed as

$$\hat{H}_v = \hat{h}_v^{(m)}(\mathbf{d}_1 \dots \mathbf{d}_m) + \hat{h}_v^{(n-m)}(\mathbf{d}_{m+1} \dots \mathbf{d}_n) + \sum_{i=1}^m \sum_{k=m+1}^n \left[-\frac{1}{m_B} \nabla_i \cdot \nabla_k + \sum_{\alpha} \frac{\hat{l}_{i,\alpha} \hat{l}_{k,\alpha}}{I_{\alpha}} \right], \quad (21)$$

where

$$\hat{h}_v^{(m)}(\mathbf{d}_1 \dots \mathbf{d}_m) \equiv \sum_{i=1}^m \left[-\frac{\nabla_i^2}{2\mu} + \sum_{\alpha} \frac{\hat{l}_{i,\alpha}^2}{2I_{\alpha}} \right] + \sum_{k>i=1}^m \left[-\frac{\nabla_i \cdot \nabla_k}{m_B} + \sum_{\alpha} \frac{\hat{l}_{i,\alpha} \hat{l}_{k,\alpha}}{I_{\alpha}} \right] + v^{(m)}(\mathbf{d}_1 \dots \mathbf{d}_m), \quad (22)$$

and an expression analogous to Eq. (22) applies to $\hat{h}_v^{(n-m)}$. The important point, evident by a consideration of Eq. (22) in the light of Eq. (17b), is that $\hat{h}_v^{(m)}$ is identical to the intermolecular Hamiltonian for the case of a cluster composed of m atoms A on one side of B and, similarly, $\hat{h}_v^{(n-m)}$ is the same as the Hamiltonian for $n-m$ atoms on one side of B. An obvious strategy for solving the $3n$ -dimensional Schrödinger equation in which Eq. (21) is the Hamiltonian is therefore to solve first the $3m$ - and $3(n-m)$ -dimensional Schrödinger equations involving $\hat{h}_v^{(m)}$ and $\hat{h}_v^{(n-m)}$, respec-

tively, and then use those solutions ($\psi_i^{(m)}$ and $\psi_j^{(n-m)}$, respectively) in a product basis to diagonalize the kinetic couplings remaining in \hat{H}_v . It is clear from Eq. (21) that the kinetic-coupling matrix elements in such a product basis are all factorizable into products of the form $\langle \psi_i^{(m)} | \hat{\delta} | \psi_j^{(m)} \rangle \times \langle \psi_j^{(n-m)} | \hat{\delta}' | \psi_j^{(n-m)} \rangle$, where $\hat{\delta}$ and $\hat{\delta}'$ are operators dependent on one or two coordinates. Thus, their evaluation is considerably more tractable than if such factorization were not possible. Notably, even if Eq. (20) is approximate and there is some small interaction between the different groups of atoms, this approach to diagonalizing \hat{H}_v can be implemented with the interaction terms handled perturbatively. Indeed, we implement such an approach in Sec. VB in application to anthracene-He₂.

III. KINETIC-ENERGY OPERATOR FOR B-A_n CLUSTERS WHEN A IS A MOLECULE

The extension of the approach of the preceding section to the case where A is a molecule is straightforward. One starts again with the classical kinetic energy apart from overall translation, which is given by

$$T = \frac{m_B}{2} \dot{\mathbf{r}}_B^2 + \frac{m_A}{2} \sum_i \dot{\mathbf{r}}_i^2 + \sum_\alpha \frac{j_\alpha^2}{2I_\alpha} + \sum_{i=1}^n \left[\sum_{\alpha_i} \frac{j_{i,\alpha_i}^2}{2I_{\alpha_i}} \right], \quad (22)$$

where symbols common to Eq. (1) are defined as for that equation except that \mathbf{r}_i now refers to the vector from the cluster center of mass to the center of mass of the *i*th A moiety, and where α_i is an index that runs over the three principal-axis directions of the *i*th A moiety, j_{i,α_i} is the component of rotational angular momentum of the *i*th moiety about its center of mass as measured along its α_i principal axis, and I_{α_i} is the moment of inertia of that moiety along that axis. It is clear that a development analogous to that leading from Eqs. (1)–(9) can be applied to Eq. (23). That is, if one defines internal coordinates \mathbf{d}_i analogously to Eq. (3), then one ultimately obtains

$$\hat{T} = -\frac{1}{2\mu} \sum_i \nabla_i^2 - \frac{1}{m_B} \sum_{k>i} \nabla_i \cdot \nabla_k + \sum_\alpha \frac{j_\alpha^2}{2I_\alpha} + \sum_{i=1}^n \left[\sum_{\alpha_i} \frac{j_{i,\alpha_i}^2}{2I_{\alpha_i}} \right], \quad (24)$$

where

$$\nabla_i \equiv \left(\frac{\partial}{\partial x_i}, \frac{\partial}{\partial y_i}, \frac{\partial}{\partial z_i} \right)$$

depends on the components of \mathbf{d}_i measured with respect to a BF axis system parallel to the principal axes of B. As with the A=atom case, though, we seek to eliminate the \hat{j}_α . To do this we substitute into Eq. (24)

$$\hat{j}_\alpha = \hat{J}_\alpha - \hat{I}_\alpha - \sum_{i=1}^n \hat{j}_{i,\alpha}, \quad (25)$$

where, as in Eq. (10), \hat{J}_α and \hat{I}_α are operators corresponding to the components along α of the total angular momentum of

the cluster and the total orbital angular momentum of the individual moieties' centers of mass about the cluster center of mass, respectively, and where $\hat{j}_{i,\alpha}$ is the operator corresponding to the component of the rotational angular momentum of the *i*th A moiety about its center of mass as measured along α . Analogously to Eqs. (17) one obtains a vibrational ($J=0$) and a rovibrational kinetic-energy operator given, respectively, by

$$\hat{T}_v = \sum_{i=1}^n \left[-\frac{\nabla_i^2}{2\mu} + \sum_\alpha \frac{(\hat{l}_{i,\alpha} + \hat{j}_{i,\alpha})^2}{2I_\alpha} + \sum_{\alpha_i} \frac{\hat{j}_{i,\alpha_i}^2}{2I_{\alpha_i}} \right] + \sum_{k>i=1}^n \left[-\frac{\nabla_i \cdot \nabla_k}{m_B} + \sum_\alpha \frac{(\hat{l}_{i,\alpha} + \hat{j}_{i,\alpha})(\hat{l}_{k,\alpha} + \hat{j}_{k,\alpha})}{I_\alpha} \right] \quad (26a)$$

and

$$\hat{T}_{rv} \equiv \sum_\alpha \frac{[\hat{J}_\alpha^2 - 2\hat{J}_\alpha \sum_i (\hat{l}_{i,\alpha} + \hat{j}_{i,\alpha})]}{2I_\alpha}. \quad (26b)$$

In Eqs. (26) the $\hat{l}_{i,\alpha}$ are given by Eq. (15). The $\hat{j}_{i,\alpha}$ and \hat{j}_{i,α_i} can be expressed in terms of the Euler angles (ϕ_i, θ_i, χ_i) that describe the orientation of the *i*th A moiety with respect to the cluster BF axes. [For example, see Eqs. (3.9) of Ref. 12 for the $\hat{j}_{i,\alpha}$ and Eqs. (3.10) of the same reference for the \hat{j}_{i,α_i} .]

Equation (26a), the analog to Eq. (17b) for molecular A moieties, is the second main result of this paper. Since we use it no further herein, we shall not give it the same scrutiny as was applied to \hat{T}_v for the A=atom case. Nonetheless, we do note that it behaves as it should for B fixed in space (infinite m_B and I_α) and that it reduces to the correct form for $n=1$ [compare with Eq. (3.12) of Ref. 12]. We also note that its structure implies that it should be possible to obtain the analog of Eq. (21) for clusters composed of different groups of A species distinguished by the lack of A–A intergroup interactions. We shall take up this point elsewhere in a study of benzene-(N₂)₂.

IV. INTERMOLECULAR LEVEL-STRUCTURE CALCULATIONS ON THE ANTHRACENE-(⁴HELIUM)₂ (1|1) ISOMER

To illustrate the application of the results of Sec. II we have performed filter diagonalization (FDG)^{22–24} variational calculations of the intermolecular level structure of the (1|1) isomer of anthracene-⁴He₂. We have also performed such calculations of the anthracene-He complex's intermolecular states, since considerable insight into the results on the $n=2$ species can be gained by detailed knowledge of the $n=1$ species' level structure. This Section outlines the procedures pertaining to these calculations.

A. Symmetry considerations, body-fixed axes

Under the assumption that He movement from one side of the aromatic plane to the other is “unfeasible,”²⁵ the molecular symmetry group of the anthracene-He₂ (1|1) isomer

TABLE I. G_8 character table for anthracene–He₂ (1|1).

Class: equivalent rotation	CL1 ^a R^0	CL2 R_z^π	CL3 R_x^π	CL4 R_y^π	CL5 R_z^π	CL6 R^0	CL7 R_y^π	CL8 R_x^π	
A'_1	1	1	1	1	1	1	1	1	$(z_1 - z_2)^b$
A'_2	1	1	-1	-1	1	1	-1	-1	R_z
B'_1	1	-1	1	-1	1	-1	1	-1	$(x_1 + x_2), T_x, \Gamma_{\text{tot}}$
B'_2	1	-1	-1	1	1	-1	-1	1	$(y_1 + y_2), T_y$
A''_1	1	1	1	1	-1	-1	-1	-1	$(z_1 + z_2), T_z$
A''_2	1	1	-1	-1	-1	-1	1	1	
B''_1	1	-1	1	-1	-1	1	-1	1	$(x_1 - x_2), R_y$
B''_2	1	-1	-1	1	-1	1	1	-1	$(y_1 - y_2), R_x, \Gamma_{\text{tot}}$

^aThe classes are as follows: CL1= E . CL2=(3,8)(4,9)(5,10)(6,11)(7,12). CL3=(3,8)(4,7)(5,6)(9,12)(10,11)*. CL4=(4,12)(5,11)(6,10)(7,9)*. CL5=(1,2)*. CL6=CL2(1,2)*. CL7=CL3(1,2)*. CL8=CL4(1,2)*. Numbers 1 and 2 refer to the helium atoms. Numbers 3–12 refer to hydrogens on anthracene. Numbering begins with the central H on the bottom of the ring and proceeds sequentially counterclockwise around the ring.

^bBF axes are defined as follows: \hat{x} is parallel to the vector that points from hydrogen No. 3 to No. 8. \hat{z} is parallel to the out-of plane symmetry axis of anthracene and always points to the side of the ring plane that He No. 1 is on. \hat{y} completes a right-handed coordinate system. T_i and R_i refer, respectively, to translation along and rotation about BF axis \hat{i} . x_1, y_1, \dots, z_2 , etc. are the coordinates of the He atoms in the BF frame (see text). Γ_{tot} denotes the irreps that the full (1|1) wavefunction must transform as.

is G_8 (isomorphic with the D_{2h} point group). The character table of G_8 applicable to this species is given in Table I. (The structure and notation of the character table matches that of Ref. 25.) In the table the permutation–inversion operations comprising the group are denoted by feasible permutations of equivalent helium and hydrogen nuclei (with parallel interchange of C atoms implied but, for clarity, not explicitly denoted). To represent permutation–inversion operations we label the helium nuclei as “1” and “2.” The hydrogen nuclei are labeled sequentially from “3” to “12” starting with a nucleus along the short in-plane axis of the anthracene moiety and proceeding counterclockwise around the anthracene ring.

The molecular symmetry group of the anthracene–He complex (for unfeasible crossing of the He from one side of the anthracene to the other) is the G_4 subgroup of G_8 (isomorphic with the C_{2v}). The character table for this group is given by the upper left quadrant of the G_8 character table of Table I. In labeling the irreducible representations (irreps) of this group we drop the primes associated with the G_8 irreps. We point out that our labeling of the BF axes (see below) and of the G_4 irreps coincides with that used by Heidenreich *et al.*¹⁴ in their study of anthracene–He intermolecular states.

To apply the results of Sec. II one requires a BF axis system parallel to the principal axes of the anthracene moiety with origin at the cluster center of mass. In labeling these axes we adopt for both species the following convention: \hat{x} is taken to be parallel to the vector that points from the center of mass of anthracene to hydrogen No. 8 (i.e., along the short in-plane axis of anthracene), \hat{z} is taken parallel to the out-of-plane principal axis of anthracene and always points to the side of the ring on which He No. 1 resides, and \hat{y} completes a right-handed coordinate system. In the notation of Table I the full rovibronic-plus-nuclear spin wave function of the (1|1) species (¹²C, ¹H, and ⁴He isotopomer) must belong to either the B'_1 or B'_2 irrep of G_8 . Since the part of the wave function that corresponds to overall rotation of the species transforms as A'_1, A'_2, B'_1 , or B'_2 and that corresponding to nuclear spin transforms as A'_1, A'_2, B'_1 , or B'_2 , the $J=0$ intermolecular states for the (1|1) isomer can transform as

any one of the eight irreps of G_8 . Similarly, the symmetry of the full wavefunction of anthracene–He must transform as B_1 or B_2 , and its rotational and nuclear-spin states transform as A_1, A_2, B_1 , or B_2 . Hence, the $J=0$ intermolecular states of the complex can transform as any one of the G_4 irreps.

B. Basis sets

For the anthracene–He₂ species a primitive basis set comprised of products of six one-dimensional discrete-variable representations (DVRs), each associated with one of the $x_1, y_1, z_1, x_2, y_2, z_2$ BF coordinates (see Sec. II), was used

$$|a, b, c, d, e, f\rangle \equiv |x_{1,a}\rangle |y_{1,b}\rangle |z_{1,c}\rangle |x_{2,d}\rangle |y_{2,e}\rangle |z_{2,f}\rangle. \quad (27)$$

Note that the position of an index on the left side of Eq. (27) has meaning: From the left the first position corresponds to the x_1 DVR, the second to the y_1 DVR, etc. The one-dimensional DVRs on the rhs of Eq. (27) are defined, as in Eq. (4.1) of Ref. 12, for example, in terms of one-dimensional harmonic-oscillator eigenfunctions (ϕ_n) and the Gauss–Hermite quadrature points and weights associated with those functions. For example, the N_x functions of the x_1 -dependent DVR are given by

$$|x_{1,a}\rangle \equiv \sum_{n=0}^{N_x-1} \sqrt{w_a} \phi_n(x_a) \phi_n(\gamma_x x_1), \quad (28a)$$

where x_a is a quadrature point, w_a is the weight associated with that point, and γ_x is chosen to tailor the DVR to the intermolecular potential-energy surface (IPS). The three remaining DVRs along the x and y axes are defined analogously. The z_1 - and z_2 -dependent DVRs differ slightly from these in that they each incorporate a second parameter ($z_{1,0}$ and $z_{2,0}$, respectively) to better accommodate the IPS. For example,

$$|z_{1,c}\rangle \equiv \sum_{n=0}^{N_z-1} \sqrt{w_c} \phi_n(z_c) \phi_n(\gamma_z [z_1 - z_{1,0}]). \quad (28b)$$

TABLE II. Basis set and inertial parameters for intermolecular-state calculation on anthracene-He and the (11) isomer of anthracene-He₂.

$N_x = 12$	$\gamma_x = 1.296\,575\ \text{\AA}^{-1}$	
$N_y = 14$	$\gamma_y = 0.956\,544\ \text{\AA}^{-1}$	
$N_z = 10$	$\gamma_z = 2.290\,773\ \text{\AA}^{-1}$	$z_{1,0} = -z_{2,0} = 3.3\ \text{\AA}$
$m_A = 4.0026\ \text{amu}$	$m_B = 178.078\ \text{amu}$	
$I_x = 1088.140\ \text{amu}\ \text{\AA}^2$	$I_y = 230.032\ \text{amu}\ \text{\AA}^2$	$I_z = 1318.173\ \text{amu}\ \text{\AA}^2$

In all cases the sizes of the two DVRs corresponding to the same BF axis were taken to be identical (e.g., N_x is the same for the x_1 and x_2 DVRs), as were the ranges of the two DVRs (as fixed by the relevant γ values). Table II gives the parameters defining the six DVRs used.

For notational convenience we adopt the following convention in regard to the labeling of the DVRs. The N functions corresponding to a given DVR are assigned integers sequentially starting with the function associated with the most negative quadrature point and ending with that associated with the most positive quadrature point. For the x - and y -dependent DVRs we take these integer labels to run from $-N/2$ to $N/2$ with zero omitted. Hence, the a and b indices run from $-N_x/2$ to $N_x/2$ (zero omitted) and b and e run from $-N_y/2$ to $N_y/2$ (zero omitted). With this convention the point \tilde{x}_{-a} ($\equiv x_{-a}/\gamma_x$), for example, equals $-\tilde{x}_a$ ($\tilde{x}_a \equiv x_a/\gamma_x$). Analogous symmetries apply to the quadrature points associated with the three other x and y DVRs. For the z -dependent DVRs, we label the functions from 1 to N_z if the relevant z_0 is positive and from $-N_z$ to -1 if the z_0 is negative. Since $z_{1,0}$ is positive and $z_{2,0} = -z_{1,0}$, the point \tilde{z}_f ($\equiv z_{2,0} + z_f/\gamma_z$) associated with the $|z_{2,f}\rangle$ DVR ($f < 0$) is equal to $-\tilde{z}_{-f}$, where \tilde{z}_{-f} ($\equiv z_{1,0} + z_{-f}/\gamma_z$) is the quadrature point associated with the $|z_{1,-f}\rangle$ DVR.

From the primitive basis set of Eq. (27), a basis set symmetry adapted to the G_4 group comprised of the first four classes of G_8 can be easily constructed. The functions are given by

$$\begin{aligned}
 &|a, b, c, d, e, f; \epsilon, \delta\rangle \\
 &= \frac{1}{2} [|a, b, c, d, e, f\rangle + (-1)^\epsilon | -a, b, c, -d, e, f\rangle \\
 &\quad + (-1)^\delta | a, -b, c, d, -e, f\rangle \\
 &\quad + (-1)^{\epsilon+\delta} | -a, -b, c, -d, -e, f\rangle], \quad (29)
 \end{aligned}$$

where ϵ and δ can take the values 0 or 1. The G_4 transformation properties of these functions are determined by the values of ϵ and δ . Since a and $-a$ refer to functions belonging to the same DVR, as do b and $-b$, d and $-d$ and e and $-e$ it is necessary to reduce the sizes of these G_4 -adapted basis sets from the full $N_x^2 \times N_y^2 \times N_z^2$ of the primitive basis to $N_x^2 \times N_y^2 \times N_z^2 / 4$ in order to eliminate redundancies. We do this by restricting the indices a and b to the ranges $-N_x/2$ to -1 and $-N_y/2$ to -1 , respectively.

The basis functions defined by Eq. (29) are those that we employ in the wave function propagations central to FDG. We do not use a fully symmetry-adapted basis in these propagations owing to difficulties in programming the operation of \hat{H}_v on a fully symmetry-adapted wave vector. Instead,

TABLE III. Allowed values of the index “ e ” for $f = -c$ and $|d| = |a|^a$

Irrep	ϵ	δ	σ	$d = a$	$d = -a$
A'_1	0	0	0	$ e \leq b $	$ e \leq b $
A'_2	1	1	0	$b \leq e < b $	$b < e \leq b $
B'_1	0	1	0	$b \leq e < b $	$b \leq e < b $
B'_2	1	0	0	$ e \leq b $	$ e < b $
A''_1	0	0	1	$ e < b $	$ e < b $
A''_2	1	1	1	$b < e \leq b $	$b \leq e < b $
B''_1	0	1	1	$b < e \leq b $	$b < e \leq b $
B''_2	1	0	1	$ e < b $	$ e \leq b $

^aSee Sec. IV B.

we impose full symmetrization during the course of the FDG procedure after the operation of \hat{H}_v (see Sec. IV D). For this final symmetrization we require expressions for fully symmetrized basis functions in terms of those of Eq. (29). These are given by

$$|a, b, c, d, e, f; \epsilon, \delta, \sigma\rangle = |a, b, c, d, e, f; \epsilon, \delta\rangle \quad (30a)$$

when $|a| = |d|$, $|b| = |e|$ and $c = -f$, and

$$\begin{aligned}
 |a, b, c, d, e, f; \epsilon, \delta, \sigma\rangle &= \frac{1}{\sqrt{2}} [|a, b, c, d, e, f; \epsilon, \delta\rangle \\
 &\quad + (-1)^\sigma |d, e, -f, a, b, -c; \epsilon, \delta\rangle] \quad (30b)
 \end{aligned}$$

for all other values of the indices. Here, $\sigma = 0$ or 1, and the values of σ , ϵ and δ completely determine the G_8 irrep to which the function belongs. For Eqs. (30) the ranges of the indices must be smaller than those that apply to Eq. (29) so as to eliminate redundancies. Several equivalent ways to eliminate redundancies are possible. We choose the following. In all cases $-N_x/2 \leq a \leq -1$, $-N_y/2 \leq b \leq -1$, $1 \leq c \leq N_z$, and $c \leq |f| \leq N_z$ apply. If $-f \neq c$, then $-N_x/2 \leq d \leq N_x/2$ and $-N_y/2 \leq e \leq N_y/2$. If $-f = c$, then $|d| \leq |a|$ in all cases and the allowed values of e depend on whether $|d| = |a|$ or not. If $-f = c$ and $|d| < |a|$, then $-N_y/2 \leq e \leq N_y/2$ in all cases. If $-f = c$ and $|d| = |a|$, the allowed values of e depend on d , b , ϵ , δ and σ , information that is summarized in Table III. Also given in Table III are the G_8 irreps that apply to the various sets of ϵ , δ , and σ values. The overall sizes of the fully symmetry-adapted bases, given the parameters in Table II, are 353 640 functions for A'_1 , 351 960 functions for A''_1 , and 352 800 functions for each of the other six irreps.

The basis set employed for calculations on anthracene-He was constructed from three-dimensional products of x_1 -, y_1 -, and z_1 -dependent DVRs [as given by Eqs. (28)]. The parameters defining the one-dimensional (1D) DVRs were taken to be the same as those employed in the $n=2$ calculations (see Table II). These primitive basis functions were symmetry-adapted to the complex's G_4 molecular symmetry group in a manner analogous to Eq. (29), giving rise to the functions

$$\begin{aligned}
|a,b,c;\epsilon,\delta\rangle \equiv & \frac{1}{2}[|a,b,c\rangle + (-1)^\epsilon|-a,b,c\rangle \\
& + (-1)^\delta|a,-b,c\rangle \\
& + (-1)^{\epsilon+\delta}|-a,-b,c\rangle], \quad (31)
\end{aligned}$$

where the notation is analogous to that used for Eq. (29). Redundancies were eliminated by restricting the indices a and b to the ranges $-N_x/2$ to -1 and $-N_y/2$ to -1 , respectively. The size of each symmetry-adapted basis is 420 functions per G_4 irrep.

C. Operation with \hat{H}_v

The (1|1) $J=0$ Hamiltonian \hat{H}_v consisted of the sum of the \hat{T}_v operator given by Eq. (17b) for $n=2$ and the pairwise-additive intermolecular potential energy function used by Heidenreich *et al.*¹⁴ in their calculations of the intermolecular level structure of the (2|0) isomer of anthracene–He₂. The values of the inertial parameters appearing in \hat{T}_v are given in Table II.

FDG requires repeated computation of the effect of operating with the Hamiltonian on a wave vector. Operation with the potential-energy portion of \hat{H}_v , $V(x_1, y_1, z_1, x_2, y_2, z_2)$, is straightforward in the basis employed herein since all the matrix elements of V are diagonal. Further, they are given (to Gaussian-quadrature accuracy) by

$$\begin{aligned}
\langle a,b,c,d,e,f;\epsilon,\delta|V|a,b,c,d,e,f;\epsilon,\delta\rangle \\
= V(\tilde{x}_a, \tilde{y}_b, \tilde{z}_c, \tilde{x}_d, \tilde{y}_e, \tilde{z}_f),
\end{aligned}$$

where \tilde{x}_a , \tilde{y}_b , etc. are defined as in Sec. IV B above. In any given FDG propagation V was calculated just once over the entire $(\tilde{x}_a, \tilde{y}_b, \tilde{z}_c, \tilde{x}_d, \tilde{y}_e, \tilde{z}_f)$ grid. The values were stored in memory to be used in the wave vector propagation.

To operate with \hat{T}_v we computed analytically the matrix elements of that operator in the basis of harmonic oscillator eigenfunctions isomorphic to the DVRs. These were then transformed to the primitive basis of Eq. (27) by using Eqs. (28) and their analogs for the other coordinates. Finally, matrix elements in the partially symmetrized basis of Eq. (29) were constructed as needed from memory-stored primitive-basis matrix elements. Unlike the potential-energy matrix, that of \hat{T}_v has nonzero off-diagonal elements. As a result, the computation time for $\hat{T}_v|\psi\rangle$ dominates in the overall computation of $\hat{H}_v|\psi\rangle$. Still, for the \hat{T}_v matrix considerable block diagonalization obtains. Indeed, nonzero matrix elements are diagonal in no less than four of the six indices characterizing the basis set. Thus, for example, the $\hat{T}_v|\psi\rangle$ calculation scales roughly as N^8 for an equal number, N , of DVRs in each dimension.

For the anthracene–He complex \hat{H}_v was taken as the sum of \hat{T}_v , as given by Eq. (17b) for $n=1$, plus the same potential-energy function as used to model the anthracene–He interaction in the $n=2$ cluster. Operation with \hat{H}_v was handled in a manner exactly analogous to that described above for the $n=2$ species.

D. Filter diagonalization

FDG was implemented by generating a random initial wave vector $|\psi_0\rangle$ in one of the four G_4 -adapted basis sets defined by Table II and by Eq. (29) (for $n=2$) or Eq. (31) (for $n=1$). The initial wave vector was propagated 512 or 1024 time steps by Chebyshev propagation.²⁶ Window basis functions filtered at selected energies within a set energy window were accumulated after each propagation step by using Eq. (6) of Ref. 24. Window basis functions obtained in this fashion are symmetry adapted to the same extent as $|\psi_0\rangle$. Hence, for the $n=1$ species no further manipulation of the window functions was required to achieve full symmetry adaptation. However, for the $n=2$ species fully symmetry-adapted window basis functions had to be calculated from the ones accumulated in the Chebyshev propagation by operating on the latter with the projection operator

$$\begin{aligned}
\hat{P}_{\epsilon,\delta,\sigma} = \sum_{\text{allstates}} |a,b,c,d,e,f;\epsilon,\delta,\sigma\rangle \\
\times \langle a,b,c,d,e,f;\epsilon,\delta,\sigma|, \quad (32)
\end{aligned}$$

with the $|a,b,c,d,e,f;\epsilon,\delta,\sigma\rangle$ given by Eqs. (30). The resulting functions were then reexpressed in the Eq. (29) basis. For both the $n=1$ and $n=2$ species the completely symmetry-adapted window functions were orthogonalized by the Gram–Schmitt method. The matrix of the relevant \hat{H}_v in this basis was then diagonalized to yield eigenvectors and eigenvalues within the chosen energy window.

In addition to the window-function variant of FDG, a time-correlation-function version^{23,24} was also applied. This was done in order to get information on \hat{H}_v eigenvalues so that the latter could then be used as energy-filter input in window-function FDG. The Chebyshev/correlation-function approach of Eqs. (12) and (13) in Ref. 24 makes direct use of the Chebyshev coefficients $c_n = \langle \psi_0|X_n\rangle$, where $|X_n\rangle$ is the Chebyshev vector obtained after n operations of a scaled \hat{H}_v on $|\psi_0\rangle$. The main point we would make here is that it is straightforward to obtain fully symmetry-factored eigenvalues from this procedure even if the propagated eigenvector is not symmetry adapted. This is done as follows. One obtains symmetry-factored Chebyshev coefficients $c_{n,\Gamma}$ by: (a) symmetrizing $|\psi_0\rangle$ with a projection operator for Γ , the irrep of interest: $\hat{P}_\Gamma|\psi_0\rangle \equiv |\psi_{\Gamma,0}\rangle$, and (b) computing $c_{n,\Gamma} = \langle \psi_{\Gamma,0}|X_n\rangle$ as the $|X_n\rangle$ are generated by the propagation of $|\psi_0\rangle$. The $c_{n,\Gamma}$ are then used in Eqs. (12) and (13) in Ref. 24 to obtain eigenvalues specific to Γ . This works because \hat{P}_Γ commutes with the scaled \hat{H}_v , $\hat{P}_\Gamma^2 = \hat{P}_\Gamma$, and Chebyshev propagation amounts to operation on the initial wave vector with a polynomial in the scaled \hat{H}_v . Hence, $\langle \psi_{\Gamma,0}|X_n\rangle$ is identical to the Chebyshev coefficient that would be computed if $|\psi_{\Gamma,0}\rangle$ were propagated instead of $|\psi_0\rangle$.

E. Rigid-body diffusion Monte Carlo calculations

As a partial check on the results of the variational calculations described above, we have performed rigid-body diffusion Monte Carlo calculations (RBDMCs)²⁷ of the zero-point energies of anthracene–He and the (1|1)

TABLE IV. Properties of computed intermolecular states for anthracene-He.

G_4 irrep	ΔE^a	$\langle z \rangle^b$	Δz	Δx	Δy	Assignment
A_1						
1	0.00	3.33	0.28	0.59	0.75	Zero point
2	13.13	3.34	0.29	0.60	1.87	$ 2\nu_y\rangle$
3	24.64	3.33	0.31	1.62	0.98	$ 2\nu_x\rangle$
4	27.99	3.37	0.30	0.69	2.26	$ 4\nu_x\rangle$
5	37.50	3.35	0.32	1.67	1.79	$ 2\nu_x, 2\nu_y\rangle$
6	41.55	3.32	0.35	1.74	2.06	$ 4\nu_x\rangle; 6\nu_y\rangle$
7	42.44	3.34	0.33	1.52	2.33	$ 4\nu_x\rangle; 6\nu_y\rangle$
8	49.03	3.74	0.52	0.90	1.11	$ \nu_z\rangle$
9	50.33	3.39	0.37	1.70	2.60	$ 2\nu_x, 4\nu_y\rangle$
10	54.46	3.39	0.34	1.00	3.39	$ 8\nu_x\rangle$
11	54.57	3.31	0.37	2.10	2.05	$ 4\nu_x, 2\nu_y\rangle$
12	60.14	3.65	0.55	1.27	2.35	$ \nu_z, 2\nu_y\rangle$
A_2						
1	21.00	3.36	0.30	1.21	1.44	$ \nu_x, \nu_y\rangle$
2	34.37	3.38	0.30	1.18	2.15	$ \nu_x, 3\nu_y\rangle$
3	38.60	3.27	0.33	2.09	1.42	$ 3\nu_x, \nu_y\rangle$
4	47.38	3.39	0.32	1.35	2.85	$ \nu_x, 5\nu_y\rangle$
5	52.54	3.32	0.34	2.06	2.32	$ 2\nu_x, 3\nu_y\rangle$
6	55.18	3.21	0.36	2.38	1.43	$ 5\nu_x, \nu_y\rangle$
7	58.38	3.34	0.36	1.62	3.44	$ \nu_x, 7\nu_y\rangle$
8	63.20	3.27	0.38	2.10	3.19	$ 3\nu_x, 5\nu_y\rangle$
9	65.64	3.84	0.55	1.46	1.55	$ \nu_z, \nu_x, \nu_y\rangle$
10	68.26	3.27	0.40	1.89	3.47	$ 3\nu_x, 7\nu_y\rangle$
B_1						
1	14.61	3.35	0.29	1.15	0.84	$ \nu_x\rangle$
2	27.49	3.37	0.30	1.18	1.81	$ \nu_x, 2\nu_y\rangle$
3	33.32	3.28	0.32	2.03	0.97	$ 3\nu_x\rangle$
4	41.16	3.39	0.31	1.25	2.47	$ \nu_x, 4\nu_y\rangle$
5	46.06	3.30	0.33	2.06	1.78	$ 3\nu_x, 2\nu_y\rangle$
6	50.10	3.23	0.36	2.35	1.14	$ 5\nu_x\rangle$
7	53.17	3.37	0.34	1.51	3.11	$ \nu_x, 6\nu_y\rangle$
8	58.17	3.34	0.39	2.05	2.68	$ 3\nu_x, 4\nu_y\rangle$
9	60.58	3.79	0.55	1.46	1.24	$ \nu_z, \nu_x\rangle$
10	62.85	3.26	0.37	2.36	1.84	$ 5\nu_x, 2\nu_y\rangle$
B_2						
1	7.71	3.35	0.29	0.62	1.48	$ \nu_y\rangle$
2	20.16	3.35	0.29	0.60	2.04	$ 3\nu_y\rangle$
3	30.41	3.33	0.31	1.70	1.42	$ 2\nu_x, \nu_y\rangle$
4	35.27	3.38	0.30	0.66	2.63	$ 5\nu_y\rangle$
5	44.11	3.37	0.33	1.67	2.26	$ 2\nu_x, 3\nu_y\rangle$
6	47.03	3.25	0.35	2.19	1.51	$ 4\nu_x, \nu_y\rangle$
7	48.33	3.39	0.33	0.88	3.23	$ 7\nu_y\rangle$
8	55.11	3.71	0.54	1.09	2.06	$ \nu_z, \nu_y\rangle$
9	55.69	3.42	0.43	1.70	2.79	$ 2\nu_x, 5\nu_y\rangle$
10	59.23	3.39	0.35	0.82	3.57	$ 9\nu_y\rangle$

^aVibrational energy in cm^{-1} . Zero-point energy is -90.52 cm^{-1} relative to dissociation.

^b $\langle z \rangle$ is the expectation value of z_1 . Δx , Δy , and Δz are, respectively, the root-mean-square deviations of x_1 , y_1 , and z_1 . All are given in Å.

anthracene-He₂ isomer for the same IPSs and inertial parameters that were employed in the variational studies. Each such calculation involved 4000 replicas. After 1000 equilibration time steps of 50 a.u., energies were averaged over 2000 or 3000 time steps of 5 a.u. The average energies corresponding to several such runs were then averaged to obtain a final result. The isomeric form of the $n=2$ species was enforced by choice of the initial replicas and by elimination of any replicas undergoing the crossing of an He atom from one side of the anthracene plane to the other (extremely rare events, in practice). The RBDMC zero-point energies so computed are $-90.3 \pm 0.4 \text{ cm}^{-1}$ for anthracene-He and

$-181.5 \pm 0.9 \text{ cm}^{-1}$ for the (1|1) species. They match those obtained variationally (Sec. V) within the precision of the RBDMC calculation.

V. COMPUTATIONAL RESULTS

A. Anthracene-He

A summary of calculated results pertaining to the intermolecular states of anthracene-He having energies less than $\sim 60 \text{ cm}^{-1}$ above the zero point ($\sim 30 \text{ cm}^{-1}$ below dissociation) is presented in Table IV. The energies and geometrical properties of the states differ slightly from those reported in

Ref. 14. There are two reasons for this. First, the basis set employed in this work is different than those of Ref. 14. The effect is a shift to lower energies (e.g., about 2 cm^{-1} for the zero-point level) for our results. Second, the Hamiltonian employed here does not treat the anthracene moiety as being fixed in space, as in Refs. 14. One consequence of accounting for anthracene motion is a level-structure shift to higher energies that partially cancels the shift due to different basis sets. Further, some states are shifted to a greater degree than others. In particular, those states involving ν_x , the vibration of the He along the x (short in-plane) axis of anthracene, have significantly higher energies above the zero-point level relative to what their energies are computed to be under the assumption of fixed-in-space anthracene. This is clearly a consequence of the fact that $\nu_x \sim \sqrt{1/\mu + \langle z_1^2 \rangle / I_y}$ ²⁸ versus $\nu_x \sim \sqrt{1/m_{\text{He}}}$ for the two cases, respectively, and the former inertial factor is significantly larger than the latter. Finally, the small differences in the expectation values of geometrical properties between the two sets of results are likely due to the difference in the way that the anthracene moiety is handled.

The assignments of anthracene–He intermolecular states presented in Table IV were made on the basis of the computed values of Δx , Δy , and Δz , as well as the nodal properties of the computed eigenfunctions. The notation employed in making the assignments accounts for three intermolecular vibrational modes, ν_x , ν_y , and ν_z , corresponding to relative motion of the He and the anthracene center of mass along the \hat{x} , \hat{y} , and \hat{z} BF axes, with the coefficient in front of ν_i denoting the number of quanta in the i th mode and with ν_i omitted completely when its coefficient is zero. One sees from the Table that the level structure is built on modes whose $1 \leftarrow 0$ fundamentals occur at 14.61, 7.71, and 49.03 cm^{-1} , for ν_x , ν_y , and ν_z , respectively. Not unexpectedly, both ν_x and ν_y are significantly anharmonic. (Undoubtedly, ν_z is, as well, though our calculations do not encompass states with two or more quanta in ν_z .) Further, there is considerable coupling between all three modes. Perhaps the most notable feature of the results, remarked upon in Ref. 14, is the marked delocalization of the He atom parallel to the anthracene plane, delocalization that increases substantially with vibrational excitation.

B. Anthracene–He₂ (1|1) isomer

Table V summarizes calculated $J=0$ intermolecular level-structure results for the (1|1) isomer of anthracene–(He)₂ for states at energies less than $\sim 30\text{ cm}^{-1}$ above the zero-point level. Also given in the table are selected expectation values and state assignments. The notation employed for the assignments reflects the fact (considered in detail below) that the (1|1) states are well approximated by zeroth-order states that are products of intermolecular eigenfunctions of the anthracene–He₁ complex:

$$|l\nu_x, m\nu_y, n\nu_z; l'\nu_x, m'\nu_y, n'\nu_z\rangle \equiv |l\nu_x, m\nu_y, n\nu_z\rangle_1 \times |l'\nu_x, m'\nu_y, n'\nu_z\rangle_2, \quad (33)$$

where the subscripts “1” and “2” refer to the He binding sites above and below the anthracene plane, and

$|l\nu_x, m\nu_y, n\nu_z\rangle_i$ is an eigenvector of anthracene–He₁ for an He atom in the i th site. For $(l, m, n) = (l', m', n')$ the functions of Eq. (33) are already symmetry adapted to G_8 . For $(l, m, n) \neq (l', m', n')$ symmetry adaptation requires constructing plus and minus linear combinations of the form

$$|l\nu_x, m\nu_y, n\nu_z; l'\nu_x, m'\nu_y, n'\nu_z\rangle_{\pm} \equiv \frac{1}{\sqrt{2}} [|l\nu_x, m\nu_y, n\nu_z; l'\nu_x, m'\nu_y, n'\nu_z\rangle \pm |l'\nu_x, m'\nu_y, n'\nu_z; l\nu_x, m\nu_y, n\nu_z\rangle]. \quad (34)$$

The notation of Eqs. (33) and (34), together with the convention that the omission of a given ν_i denotes zero quanta in that mode and that “0” denotes $0\nu_x$, $0\nu_y$, $0\nu_z$, is what appears for assignments in Table V. Thus, for example, the $1B'_1$ state is assigned as

$$|\nu_y; 0\rangle_+ \equiv \frac{1}{\sqrt{2}} [|\nu_y\rangle_1 |0\rangle_2 + |0\rangle_1 |\nu_y\rangle_2]$$

in which one quantum of ν_y is shared in-phase between the two He atoms. Similarly, the $1B''_1$ state is assigned as

$$|\nu_y; 0\rangle_- \equiv \frac{1}{\sqrt{2}} [|\nu_y\rangle_1 |0\rangle_2 - |0\rangle_1 |\nu_y\rangle_2]$$

in which one quantum of ν_y is shared out-of-phase between the He atoms.

The close connection between (1|1) anthracene–He₂ and anthracene–He₁ intermolecular states arises because the six-dimensional IPS of the former species is the sum of two three-dimensional terms that are each the same as the anthracene–He₁ IPS plus a very much smaller six-dimensional He–He interaction term V_{12} . Therefore, given Eq. (21), \hat{H}_v for the $n=2$ species is the sum of two $n=1$ Hamiltonians plus V_{12} plus the kinetic coupling term

$$\hat{T}_{12} \equiv -\frac{1}{m_B} \nabla_1 \cdot \nabla_2 + \sum_{\alpha} \frac{\hat{l}_{1,\alpha} \hat{l}_{2,\alpha}}{I_{\alpha}}. \quad (35)$$

The product basis defined by Eq. (33) diagonalizes $\hat{H}_v - \hat{T}_{12} - V_{12}$. Hence, that basis provides a good representation of the (1|1) states to the extent that $\hat{T}_{12} + V_{12}$ is small compared to the rest of \hat{H}_v .

To investigate quantitatively the $n=1$ composition of the (1|1) intermolecular states, and to assess the suitability of the approach outlined at the end of Sec. II for the solution of intermolecular Schrödinger equations, we have calculated the (1|1) states variationally by using the Eq. (33)/(34) basis. This was done as follows. The eigenvectors corresponding to the 42 $n=1$ states enumerated in Table IV were used to construct product basis functions as per Eqs. (33) and (34). The 1764 resulting functions divide amongst the G_8 irreps as 243 A'_1 , 201 A''_1 , and 220 for each of the other six. For each irrep the matrix of \hat{H}_v was constructed in the product basis under the assumption of negligible off-diagonal V_{12} matrix elements. Off-diagonal elements of \hat{T}_{12} were taken fully into account. Finally, the symmetry-factored matrices were diago-

TABLE V. Properties of computed intermolecular states for the (1|1) isomer of anthracene–He₂.

G_8 irrep	ΔE^a	$\langle z \rangle^b$	Δz	Δx	Δy	Assignment
A_1'						
1	0.0	3.33	0.28	0.59	0.76	Zero-point
2	13.13	3.34	0.29	0.59	1.43	$ 2\nu_y;0\rangle_+$
3	15.43	3.35	0.29	0.62	1.48	$ \nu_y;\nu_y\rangle$
4	24.06	3.33	0.29	1.20	0.86	90% $ 2\nu_x;0\rangle_+$; 9% $ \nu_x;\nu_x\rangle$
5	26.23	3.35	0.29	0.60	1.87	$ 2\nu_y;2\nu_y\rangle$
6	27.78	3.35	0.29	0.62	1.74	44% $ 4\nu_y;0\rangle_+$; 54% $ 3\nu_y;\nu_y\rangle_+$
7	28.03	3.35	0.29	0.63	1.73	52% $ 4\nu_y;0\rangle_+$; 45% $ 3\nu_y;\nu_y\rangle_+$
8	29.68	3.35	0.29	1.17	0.87	8% $ 2\nu_x;0\rangle_+$; 87% $ \nu_x;\nu_x\rangle$
A_1''						
1	13.13	3.34	0.29	0.59	1.43	$ 2\nu_y;0\rangle_-$
2	24.60	3.33	0.30	1.22	0.87	$ 2\nu_x;0\rangle_-$
3	27.79	3.35	0.29	0.62	1.76	54% $ 4\nu_y;0\rangle_-$; 84% $ 3\nu_y;\nu_y\rangle_-$
4	28.07	3.35	0.29	0.63	1.72	84% $ 4\nu_y;0\rangle_-$; 54% $ 3\nu_y;\nu_y\rangle_-$
A_2'						
1	20.43	3.35	0.29	0.93	1.16	77% $ \nu_x;\nu_y,0\rangle_+$; 22% $ \nu_x;\nu_y\rangle_+$
2	22.87	3.35	0.29	0.95	1.19	22% $ \nu_x;\nu_y,0\rangle_+$; 77% $ \nu_x;\nu_y\rangle_+$
A_2''						
1	20.52	3.35	0.29	0.93	1.16	79% $ \nu_x;\nu_y,0\rangle_-$; 21% $ \nu_x;\nu_y\rangle_-$
2	22.72	3.35	0.29	0.95	1.19	21% $ \nu_x;\nu_y,0\rangle_-$; 79% $ \nu_x;\nu_y\rangle_-$
B_1'						
1	13.58	3.34	0.29	0.90	0.79	$ \nu_x;0\rangle_+$
2	26.58	3.35	0.29	0.91	1.42	56% $ \nu_x,2\nu_y,0\rangle_+$; 43% $ \nu_x,2\nu_y\rangle_+$
3	27.78	3.36	0.29	0.94	1.46	$ \nu_y;\nu_x+\nu_x\rangle_+$
4	28.57	3.35	0.29	0.95	1.42	43% $ \nu_x,2\nu_y,0\rangle_+$; 56% $ \nu_x,2\nu_y\rangle_+$
B_1''						
1	15.57	3.34	0.29	0.94	0.80	$ \nu_x;0\rangle_-$
2	26.60	3.35	0.29	0.91	1.42	56% $ \nu_x,2\nu_y,0\rangle_-$; 44% $ \nu_x,2\nu_y\rangle_-$
3	28.56	3.35	0.29	0.95	1.42	43% $ \nu_x,2\nu_y,0\rangle_-$; 55% $ \nu_x,2\nu_y\rangle_-$
4	29.63	3.36	0.29	0.98	1.46	$ \nu_y;\nu_x,\nu_y\rangle_-$
B_2'						
1	7.65	3.34	0.28	0.60	1.17	$ \nu_y;0\rangle_+$
2	20.14	3.34	0.29	0.59	1.55	$ 3\nu_y;0\rangle_+$
3	20.77	3.35	0.29	0.61	1.68	$ 2\nu_y;\nu_y\rangle_+$
4	30.08	3.33	0.30	1.25	1.14	$ 2\nu_x,\nu_y;0\rangle_+$
B_2''						
1	7.78	3.34	0.28	0.60	1.18	$ \nu_y;0\rangle_-$
2	20.15	3.34	0.29	0.59	1.55	$ 2\nu_y;0\rangle_-$
3	20.95	3.35	0.29	0.61	1.69	$ 2\nu_y;\nu_y\rangle_-$
4	30.11	3.33	0.30	1.26	1.14	$ 2\nu_x,\nu_y;0\rangle_-$

^aVibrational energy in cm^{-1} . Zero-point energy is -181.09 cm^{-1} relative to dissociation.

^b $\langle z \rangle$ is the expectation value of z_1 . Δx , Δy , and Δz are, respectively, the root-mean-square deviations of x_1 , y_1 , and z_1 from their expectation values. All are given in Å.

nalized numerically. The differences between energies obtained by this procedure and those obtained by diagonalizing the full \hat{H}_v in the 6D DVR basis (Table V) differ from one another by only 0.01 cm^{-1} (root mean squared). Obviously, there is excellent agreement between the two sets of results. This agreement clearly points the way to the assignment of the cluster's intermolecular states in terms of the product basis states. The assignments given in Table V are based on quantitative analysis of the product-basis-state composition of the intermolecular eigenvectors obtained from the calculation just described. (All basis states contributing 8% or more to an eigenstate are listed in the table.) The agreement is also significant in that the calculation based on the anthracene–He₁ product basis is much less costly than the full six-dimensional calculation of (1|1) states. This is because: (a) the only off-diagonal elements involved in the former are those of \hat{T}_{12} , and each such matrix element can

be factored into two three-dimensional integrals, and (b) the product basis states are excellent zeroth-order approximations of the true eigenstates, so that convergence of lower-lying states in a variational calculation can be achieved with a relatively small basis. The (1|1) species is thus a good case in point illustrating that accurate results can be obtained with considerably reduced computational effort by using the general approach discussed at the end of Sec. II.

In regard to the details of the calculated (1|1) level structure, one notes the presence of three types of eigenstates. First, there are those (“type one”) that are essentially pure zeroth-order states of the Eq. (33)/(34) type with vibrational energies that are almost identical to those of their counterpart states in anthracene–He. Two examples are $2A_1'$ (99.7% $|2\nu_y;0\rangle_+$) and $1A_1''$ (99.9% $|2\nu_y;0\rangle_-$), which are both at 13.13 cm^{-1} in the (1|1) species compared with the 13.13 cm^{-1} vibrational energy of $|2\nu_y\rangle$ in anthracene–He. Second,

there are also states (“type two”) that are pure Eq. (33)/(34) states but that have vibrational energies that deviate appreciably from those of anthracene–He states. For example, $1B'_2$ is 99.7% $|\nu_x;0\rangle_+$ but has vibrational energy $\sim 1\text{ cm}^{-1}$ lower than the $|\nu_x\rangle$ anthracene–He state. Similarly, $1B''_2$ is 99.8% $|\nu_x;0\rangle_-$ but has vibrational energy $\sim 1\text{ cm}^{-1}$ above that of $|\nu_x\rangle$. Third, there are states (“type three”) that have significant contributions from more than one Eq. (34)/(35) function. Two such states are $6A'_1$ and $7A'_1$.

The source of the difference between these three classes of (1|1) states relates to the magnitude of off-diagonal matrix elements of \hat{T}_{12} in the basis of the anthracene–He product states of Eq. (33). Expressing a general such matrix element as

$$\langle L\nu_x, M\nu_y, N\nu_z; L'\nu_x, M'\nu_y, N'\nu_z | \hat{T}_{12} | l\nu_x, m\nu_y, n\nu_z; l'\nu_x, m'\nu_y, n'\nu_z \rangle \quad (36)$$

one can readily show from Eq. (35) and knowledge of harmonic-oscillator matrix elements that it will generally be appreciable in just three cases: (a) when $|l-L|=|l'-L'|=1$, $(m-M)=(m'-M')=(n-N)=(n'-N')=0$; (b) when $|m-M|=|m'-M'|=1$, $(l-L)=(l'-L')=(n-N)=(n'-N')=0$; and (c) when $|n-N|=|n'-N'|=1$, $(l-L)=-|l'-L'|=(m-M)=(m'-M')=0$. A type-one state corresponds to a product state that is not nearby in zeroth-order energy to any other such state that can satisfy these approximate selection rules. As a result the product state itself is essentially a (1|1) eigenstate, and its vibrational energy is very close to its zeroth-order (anthracene–He) energy. Going back to the examples of the type-one states $2A'_1$ and $1A''_1$, $|\nu_y; \nu_y\rangle$ is the product state closest in energy to $|2\nu_y;0\rangle$ and its degenerate partner $|0;2\nu_y\rangle$ that can also couple with the latter two according to the selection rules above. However, it is 2.3 cm^{-1} higher in energy, a separation that apparently is too large to allow for effective coupling. The upshot is that the two symmetry-adapted combinations of $|2\nu_y;0\rangle$ and $|0;2\nu_y\rangle$ are (1|1) eigenstates with vibrational energies almost equal to one another as well as to that of $|2\nu_y\rangle$.

Type-two states arise when the only other product state in the vicinity of product state $|l\nu_x, m\nu_y, n\nu_z; l'\nu_x, m'\nu_y, n'\nu_z\rangle$ that can also satisfy the selection rules to couple with it is its zeroth-order-degenerate partner $|l'\nu_x, m'\nu_y, n'\nu_z; l\nu_x, m\nu_y, n\nu_z\rangle$. The coupling between the two states leads to plus and minus linear combinations that are essentially (1|1) eigenstates. The vibrational energies of these eigenstates can deviate appreciably from anthracene–He energies due to the coupling. As a case in point, the $1B'_2$ and $1B''_2$ type-two examples given above arise from the product states $|\nu_x;0\rangle$ and $|0;\nu_x\rangle$. There are no other product states close in zeroth-order energy to these two that can also couple effectively with them according to the selection rules above. However, coupling between the two themselves is allowed, leading to plus and minus combinations with vibrational energies below and above that of $|\nu_x\rangle$.

Finally, type-three states arise when appreciable coupling is allowed between nearby, though nondegenerate, product states. The result of such coupling is a set of eigen-

states that have significant admixtures from more than one zeroth-order state and vibrational energies that deviate from anthracene–He energies. As examples, the product states $|4\nu_y;0\rangle$ and $|3\nu_y; \nu_y\rangle$ have zeroth-order energies about 0.1 cm^{-1} apart and can couple with one another according to the selection rules above. The same situation applies to $|0;4\nu_y\rangle$ and $|\nu_y;3\nu_y\rangle$. The coupling gives rise to the four, type-three states $6A'_1$, $7A'_1$, $3A''_1$, and $4A''_1$, each of which is an admixture of the four product states.

VI. CONCLUSION

We have presented expressions for the intermolecular kinetic-energy operators of solute–solvent_n clusters of the type B–A_n, where A is an atom or a molecule and B is a molecule. The operators are expressed in terms of coordinates referred to a body-fixed frame that is embedded in the B moiety. As such, they are valuable in intermolecular level-structure calculations involving clusters wherein: (i) A–B interactions tend to dominate over A–A interactions and/or (ii) B is significantly larger than A. As an illustration of the application of the results we have performed 6D variational calculations of the intermolecular states of the anthracene–He₂ (1|1) isomer for the IPS of Heidenreich *et al.*¹⁴ We have shown that these states can be readily assigned in terms of products of anthracene–He₁ intermolecular eigenfunctions, assignments that are especially transparent given the form of the intermolecular Hamiltonian employed. Finally, we have outlined a procedure that substantially decreases the cost of calculations of intermolecular states in B–A_n clusters containing subsets of A moieties that do not interact appreciably with one another. We have demonstrated the application of this procedure in calculations on the anthracene–He₂ (1|1) isomer.

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