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Application of a diabatic distorted wave approximation to the study of $X \cdot \cdot H_2$ ($X = He, Ne, Ar$) van der Waals molecules

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A diabatic rotational decoupling scheme is applied to $X \cdot \cdot H_2$ van der Waals molecules using the anisotropic potentials of Tang and Toennies [J. Chem. Phys. **68**, 5501 (1978); **74**, 1148 (1981)]. We have developed the method proposed by Beswick and Requena [J. Chem. Phys. **72**, 3018 (1980)] in an entirely numerical way. Attention is focused on the rotational predissociating levels and on the shape resonances of these systems. Among these resonances, a narrow orbiting and narrow overbarrier resonances are found for the complexes $Ne-H_2$ and $Ar-H_2$, respectively. They should be amenable to experimental observation in molecular beam scattering as well as infrared spectroscopic studies.

INTRODUCTION

Weakly bound rare gas- H_2 systems are of considerable interest in the context of van der Waals (vdW) molecules. Recently a great amount of experimental information about these systems has become available. Knowledge of these experimental results is very important for the determination and understanding of intermolecular forces in the region of the attractive well.

In the present paper, we envisage the fragmentation of the He, Ne, Ar- H_2 vdW molecules occurring when the diatomic subunit is rotationally excited. Thus, within a diabatic picture, we can recognize two different mechanisms: (a) if the metastable level is coupled to a family of continua, due to the anisotropy of the vdW interaction, the complex dissociates by rotational predissociation (RP). This process takes place by transference of an excess of internal rotational energy from H_2 towards the weak bond, leading eventually to its breaking up. And, (b) if the metastable level interacts with its continuum, the fragmentation occurs directly. Such metastable levels, called shape resonances, are associated to potential energy barriers. It can be distinguished into two classes: the orbiting resonances, which are located under the top of the barrier, and the overbarrier resonances. In both mechanisms, the relevant quantities are the energy position of the metastable level and its associated width. Experimental widths for RP have only been reported for the Ar-HD and Kr- H_2 complexes.¹ However, the RP process has been suggested in connection with broadening features found in the infrared spectra of many other systems.^{1,2} Also, in the experimental observations with crossed molecular beams, the vdW metastable states cause perturbations in the energy dependence of the various scattering cross sections³ and therefore are amenable, in principle, to direct detection. In this way, infrared spectra^{1,2(a)-2(c)} and molecular beam scattering studies^{4,5} on rare gas- H_2 systems have greatly contributed to the understanding of the features of the corresponding vdW interactions.

On the other hand, from the theoretical point of view, two kinds of related problems must be overcome in order to study these systems. The first one concerns the determination of the intermolecular potentials. Although there are a

great amount of computational problems in order to determine these potentials, some *ab initio*,⁶ semiempirical,^{7,8} or completely empirical potentials⁹ are available now. The second problem is related to the dynamics of dissociation for which "exact" and several approximate methods have been proposed. The aim of these approximate methods is mainly twofold, to provide physical pictures of the process and to avoid the excessive computational effort of the exact calculations. Moreover, they can also provide reliable empirical potential surfaces.

Among the different approaches for treating the RP process of these complexes, we want to stress two efficient methods: (1) the secular equation (SE) method,¹⁰ recently improved by adding perturbation theory (PT),¹¹ that yields results in very good agreement with the exact ones,^{16(a)} and (2) the diabatic rotational distorted wave (DRDW) method,¹² that leads to sufficiently precise results when it is developed in an entirely numerical way,¹³ but involving less computational effort. In the second method, the Hamilton is represented in an angular basis and, taking advantage of the large rotational spacing of the H_2 molecule, only the diagonal elements are considered in order to obtain zero-order discrete and continuum solutions. After that, discrete-continuum coupling through the nondiagonal matrix elements are used to estimate widths for the RP process within the "Golden Rule" framework. This decoupling scheme, as proposed by Beswick and Requena,¹² was developed in an analytical way.

In this work, our objective has been the numerical application of the DRDW approximation to the study of $X-H_2$ systems ($X = He, Ne, Ar$). We investigate rotational predissociating levels and also, as a straightforward extension, shape resonances on a single channel corresponding to a unique diatomic rotational state. We shall restrict ourselves to the particular case of $J = 0$, J being the total angular momentum. We have chosen the semiempirical potentials proposed by Tang and Toennies (TT).⁷ As these authors point out, these potentials are found to work fairly well in the attractive and repulsive regions, yielding cross section anisotropy factors in agreement with experiment. The TT potentials describe the interaction of a rare gas atom and the H_2

molecule considered like a rigid rotor. The diatomic bond length is frozen at its averaged value in the ground vibrational state. Therefore, the process of vibrational predissociation (VP) is neglected. This is a reasonable point, since it has been shown¹⁴ that for these molecules the VP process is very slow as compared with the dissociation mechanisms studied here. Also, close coupling calculations for the He + H₂ collision¹⁵ have confirmed this tendency showing low vibrational relaxation cross sections. However, the rotational predissociating levels and their associated widths have been found to be strongly dependent on the diatomic vibrational excitation.^{10(c)} This fact must be taken into account in order to do a proper comparison between theoretical results and spectroscopic data.

We start the presentation of the results with a comparison between the two versions, analytical or numerical, of the DRDW approach. Then, we report energy positions and half-widths for the RP process, using the TT potentials. For Ar-H₂, a very good agreement with available exact results¹⁶ is found. This indicates the small contribution arising from discrete-discrete and continuum-continuum couplings, that are neglected in our treatment. Concerning shape resonances, we have searched only the first one appearing on each rotational channel investigated. As expected, the associated widths are larger than those of rotational predissociating levels. However, a narrow orbiting resonance for Ne-H₂ and a narrow overbarrier one for Ar-H₂ were found. The lifetime of this last resonance is about 6.7 ps. This interesting result has been verified by means of close-coupling calculations. At the same time, in both types of quasibound levels, and for the Ar-H₂ complex, we have studied the reliability of the corresponding TT potential. We have obtained an overestimate of the energy positions of ~ 1 cm⁻¹ as compared with experiment. All these results are reported and discussed in the last section.

II. THEORETICAL TREATMENT

We are interested in X · · H₂ van der Waals molecules where X = He, Ne, Ar, and the diatomic molecule is treated like a rigid rotor rotational constant B_e. After separation of the center-of-mass motion of the whole system, the Hamiltonian for nuclear motion on a single electronic potential energy surface may be written as^{9(c),16}

$$H = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{\hbar^2 \mathbf{l}^2}{2\mu R^2} + B_e j^2 + V(R, \gamma), \quad (1)$$

where μ is the atom-diatom reduced mass, R is the distance between X and the H₂ center of mass, γ is the angle between the R vector and the vector corresponding to the H₂ bond, r, while l and j are angular momentum operators associated to R and r, respectively. In Eq. (1) V(R, γ) describes the van der Waals interaction. It goes to zero as R goes to infinity whatever be the orientation γ.

For J and M quantum numbers given, associated to the total angular momentum J = j + l and its third component in a space-fixed representation, respectively, the Schrödinger equation

$$H |\Psi^{JM}(\mathbf{R}, \hat{r})\rangle = E |\Psi^{JM}(\mathbf{R}, \hat{r})\rangle \quad (2)$$

may be solved by expanding the wave function in a body-fixed angular basis¹⁷

$$|\Psi^{JM}(\mathbf{R}, \hat{r})\rangle = \sum_{j, \Omega} \phi_{j\Omega}^{JM}(R) |JMj\Omega\rangle, \quad (3)$$

where \hat{r} is the unit vector in the r direction, j is the rotational quantum number associated to j and referred to the body-fixed system of coordinates, while Ω is the “tumbling” angular momentum quantum number corresponding to the projection of J on the R direction. Substitution of Eq. (3) into Eq. (2) leads, after scalar multiplication by |JMj'Ω'⟩, to the following set of coupled equations:

$$\left\{ -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + B_e j(j+1) + V_{j\Omega, j\Omega}^{JM}(R) - E \right\} \phi_{j\Omega}^{JM}(R) = \sum_{j', \Omega'} V_{j\Omega, j'\Omega'}^{JM}(R) \phi_{j'\Omega'}^{JM}(R), \quad (j'\Omega') \neq (j, \Omega), \quad (4)$$

where the potential matrix elements are

$$V_{j\Omega, j'\Omega'}^{JM}(R) = \langle JMj\Omega | \left[V(R, \gamma) + \frac{\hbar^2 \mathbf{l}^2}{2\mu R^2} \right] | JMj'\Omega' \rangle. \quad (5)$$

Henceforth, the superscripts JM drop out for simplicity.

Diabatic approach consists in neglecting all the off-diagonal terms in Eq. (4), solving in zero order the uncoupled equations

$$\left\{ -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + V_{j\Omega, j\Omega}(R) + B_e j(j+1) - E \right\} \phi_{j\Omega}^{(0)}(R) = 0; \quad (6)$$

Eq. (6) has discrete as well as continuum solutions.¹² Discrete solutions are obtained by solving

$$\left\{ -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + V_{j\Omega, j\Omega}(R) - \epsilon_{j\Omega, v} \right\} \phi_{j\Omega, v}^{(0)}(R) = 0, \quad (7)$$

where v is a quantum number associated to the van der Waals stretching and ε_{jΩ, v} < 0. Actual triatomic energy is

$$E_{j\Omega, v} = \epsilon_{j\Omega, v} + B_e j(j+1)$$

and the corresponding state may be a bound or quasibound (metastable) state.

On the other hand, continuum solutions are obtained from the equation

$$\left\{ -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + V_{j\Omega, j\Omega}(R) - \epsilon \right\} \phi_{j\Omega, \epsilon}^{(0)}(R) = 0, \quad (8)$$

where ε > 0 represents the relative kinetic energy between the fragments, E = ε + B_ej(j+1) being the total energy. The functions φ_{jΩ, ε}⁽⁰⁾(R) are chosen to be energy normalized.

Now, within the simplest Golden Rule framework, the half-width for rotational predissociation associated to the (jΩ, v) quasibound state is given by

$$\Gamma_{j\Omega, v} = \pi \sum_{j' < j} |\langle \phi_{j\Omega, v}^{(0)}(R) | V_{j\Omega, j'\Omega'}(R) | \phi_{j'\Omega', \epsilon}^{(0)}(R) \rangle|^2, \quad (9)$$

where each contribution must be calculated “on-shell energy,” i.e., for

$$\epsilon = \epsilon_{j\Omega, v} + B_e [j(j+1) - j'(j'+1)].$$

Also, from Eq. (8), we may search shape resonances on

each channel labeled by ($j\Omega$). It is well known that, asymptotically, continuum wave functions behave as

$$\phi_{j\Omega;\epsilon}^{(0)}(R) \underset{R \rightarrow \infty}{\sim} A \sin\{kR + \delta_{j\Omega}(\epsilon)\}, \quad (10)$$

where $k = (2\mu\epsilon)^{1/2}/\hbar$ is the wave number, $A = (2\mu/\pi k)^{1/2}/\hbar$ is the normalization factor, and $\delta_{j\Omega}$ the phase shift. Near a resonance, this quantity takes the Breit-Wigner form¹⁸

$$\delta_{j\Omega}(\epsilon) = \delta_{j\Omega}^{(0)}(\epsilon) + \arctan\left\{\frac{\Gamma_{j\Omega}}{2(\epsilon_{j\Omega} - \epsilon)}\right\},$$

where $\epsilon_{j\Omega}$ denotes the resonance position while $\Gamma_{j\Omega}$ stands for its corresponding width; $\delta_{j\Omega}^{(0)}$ is a background contribution that, for narrow and isolated resonances, becomes smooth as a function of the energy. Hence, the cross section

$$\sigma_{j\Omega}(\epsilon) = \frac{4\pi}{k^2} (2j+1) \sin^2 \delta_{j\Omega}(\epsilon) \quad (11)$$

looks, near a resonance, as a Lorentzian or Fano-type function depending on the local value of the background $\delta_{j\Omega}^{(0)}$ at the resonance energy.

III. RESULTS AND DISCUSSION

Usually, the van der Waals interaction is described by an expansion in terms of Legendre polynomials $P_\lambda(\cos \gamma)$ as follows:

$$V(R, \gamma) = \sum_\lambda V_\lambda(R) P_\lambda(\cos \gamma). \quad (12)$$

Hence, potential matrix elements $V_{j\Omega, j'\Omega'}(R)$, Eq. (5), may be analytically calculated from the well-known matrix elements of $P_\lambda(\cos \gamma)$ and l^2 in the body-fixed representation.^{17(b)} In this work, we have assumed a total angular momentum $J = 0$, that implies a projection on the Z space-fixed axis $M = 0$ and a tumbling quantum number $\Omega = 0$. Therefore the necessary matrix elements are reduced to the following:

$$\begin{aligned} \langle 00j0 | l^2 | 00j'0 \rangle &= \delta_{jj'} j(j+1), \\ \langle 00j0 | P_\lambda(\cos \gamma) | 00j'0 \rangle &= [(2j'+1)/(2j+1)]^{1/2} \\ &\quad \times C^2(j'0\lambda 0 | j'\lambda j0), \end{aligned}$$

where $C(j_1 m_1 j_2 m_2 | j_1 j_2 j_3 m_3)$ are Clebsch-Gordan coefficients.¹⁹

To obtain bound and rotational predissociating triatomic levels, we have numerically solved Eq. (7) using the

Truhlar's algorithm.²⁰ Essentially, it consists in expanding the wave function as a Taylor series up to the second order. Usual boundary conditions lead to a tridiagonal matrix whose diagonalization provides the desired eigenvalues and eigenfunctions in an efficient way.²¹

Similarly, continuum wave functions were obtained by numerical solution of Eq. (8). We have employed a Fox-Numerov algorithm²² of propagation and evaluated the phase shift by using the expression (10). Hence, shape resonances were investigated through the behavior of the cross section, Eq. (11), as a function of the relative kinetic energy ϵ .

Also, application of the Golden Rule approximation, Eq. (9), was carried out by standard numerical quadrature after the discrete states, the continua and the relevant coupling were determined.

Assuming a rotational diatomic constant $B_e = 60.81 \text{ cm}^{-1}$ and using the Dunker and Gordon potentials for Ne-H₂ and Ar-H₂, a comparison between our numerical results and the analytical ones¹² is shown in Table I. As it can be seen, both types of calculations give rise to similar results for the rotational predissociating levels investigated. This agreement was also obtained in a previous work on the He-HF system.¹³ However, in the Ne-H₂ molecule we have not found any level corresponding to a diatomic rotational quantum number $j = 4$, in contrast with the analytic result. In fact, the analytic method introduces a spurious term in the diagonal potentials $V_{j\Omega, j\Omega}(R)$ when the Pekeris' procedure²³ is followed [see Eq. (28c) of Ref. 12]. Thus, an energy of 1224.2 cm^{-1} , higher than the diatomic rotational energy $B_e \times 4 \times 5 = 1216.2 \text{ cm}^{-1}$, was reported.¹² Therefore, that energy does not correspond to an actual quasibound level, but is an artifact of the analytical calculations.

As we already mentioned, more accurate potentials for some X-H₂ systems can be found in the literature; however, for the purpose of comparison among the system studied here, it is convenient to use the anisotropic potentials of Ref. 7. They are expressed by two terms in the Legendre expansion (12) as

$$V(R, \gamma) = V_0(R) + V_2(R) P_2(\cos \gamma)$$

and the rigid rotor H₂ is assumed to have a bond length equal to the corresponding expectation value on the ground vibrational state.⁷ Hence, the rotational constant of the diatomic subunit takes a value of $B_e = 56.90 \text{ cm}^{-1}$.

Up to a diatomic rotational excitation $j = 5$, bound and

TABLE I. Energies E and half-widths Γ in cm^{-1} numerically calculated for some rotational predissociating levels of X...H₂ (X = Ne, Ar) van der Waals molecules. They correspond to the stretching quantum number $v = 0$ and are compared with the analytical results of Ref. 12. The same potentials [Ref. 9(c)] were used in both calculations, assuming a rotational diatomic constant $B_e = 60.81 \text{ cm}^{-1}$.

| | Ne...H ₂ | | Ar...H ₂ | |
|---------|--|---|--|--|
| | Ref. 12 | This work | Ref. 12 | This work |
| $j = 2$ | $E = 364.5$ $\Gamma = 0.51 \times 10^{-2}$ | $E = 363.7$ $\Gamma = 0.40 \times 10^{-2}$ | $E = 347.2$ $\Gamma = 0.77 \times 10^{-2}$ | $E = 346.9$ $\Gamma = 0.72 \times 10^{-2}$ |
| $j = 4$ | $E = 1224.2$ $\Gamma = 0.14 \times 10^{-3}$ | ... | $E = 1206.6$ $\Gamma = 0.37 \times 10^{-3}$ | $E = 1206.1$ $\Gamma = 0.33 \times 10^{-3}$ |

rotational predissociating levels for Ne-H₂ and Ar-H₂ are shown in Table II. These levels were not found in the He-H₂ system. All these states correspond to negative eigenvalues $\epsilon_{j,0}$ in Eq. (7). Because of the Legendre expansion taken for the potentials, rotational predissociation occurs with a variation of the diatomic rotational state $\Delta j = -2$. So that, triatomic levels for which $j = 0, 1$ cannot predissociate and become bound levels. After $j = 3$ and $j = 6$, for Ne-H₂ and Ar-H₂, respectively, the corresponding effective diagonal potentials do not support discrete levels. When the results shown in this table are compared with those of Table I, large differences in energies and a factor about 2 in half-widths can be observed for both systems. This discrepancy is similar to that reported by Le Roy *et al.*^{10(c)} Moreover, when we compare energy position and half-width corresponding to Ar-H₂ ($J = 0, j = 2$) with those obtained by a complex-coordinate coupled channel (CCCC) formalism¹⁶ using the same potential surface,^{7(b)} a good agreement is found. Thus, with the rotational constant $B_e = 60.853 \text{ cm}^{-1}$ of that work instead of the value 56.90 cm^{-1} assumed here, we get $E = 346.172 \text{ cm}^{-1}$ and $\Gamma = 0.13 \times 10^{-1} \text{ cm}^{-1}$, while the CCCC values are 346.1433 and $0.127 \times 10^{-1} \text{ cm}^{-1}$, respectively. It may be stressed that the width reached within the present approach is accurate to 2%–3%, while the level energy shows an error of 0.03 cm^{-1} . Larger differences were found¹⁶ depending on the potential surface chosen. In fact, using the Buckingham–Corner potential of Le Roy and Carley,^{9(d)} that is probably the most realistic potential for Ar-H₂, the results of CCCC calculations are $E = 345.3871 \text{ cm}^{-1}$ and $\Gamma = 0.0158 \text{ cm}^{-1}$ for the same $J = 0, j = 2$ level. Therefore, for the Ar-H₂ complex, the Tang and Toennies potential yields errors in energy position of rotational predissociating levels of about 1 cm^{-1} . Anyway, from Table II, we realize that the general features pointed out in Ref. 12 are held. For the only comparable level, the half-width in Ne-H₂ is lower than in Ar-H₂. This quantity, for Ar-H₂, decreases as j increases showing the gradual dynamical decoupling between diatomic rotation and the van der Waals stretching motion.

Energy positions and widths associated to some shape resonances are listed in Table III for the three systems under consideration. They were obtained within the single channel

TABLE III. Energies and widths, in cm^{-1} , for shape resonances of X-H₂ systems ($X = \text{He, Ne, Ar}$). Except that marked with an asterisk, all of them correspond to overbarrier resonances. Because of the asymmetry found in most of them, we report the associated total width (full width at half of the maximum cross section).

| j | He-H ₂ | | Ne-H ₂ | | Ar-H ₂ | |
|-----|-------------------|-------|-------------------|-------|-------------------|-------|
| | Energy | Width | Energy | Width | Energy | Width |
| 2 | 345.22 | 4.67 | 346.58 | 7.64 | 341.91 | 0.79 |
| 3 | | | 683.78* | 0.13 | 684.75 | 2.81 |
| 4 | | | 1142.94 | 3.97 | 1142.07 | 4.59 |
| 5 | | | | | 1713.66 | 6.58 |

diabatic approach, and correspond to the first resonance found at each j value investigated. The cross sections calculated by means of Eq. (11) look, in most cases, like asymmetric Lorentzian functions of the energy. Hence, we report the full widths estimated at half of the corresponding maximum cross section. For He-H₂, wide overbarrier resonances were obtained. Moreover, due to the small well-depth of this system, the effective potential for $j = 3$ already presents a positive minimum. Concerning Ne-H₂, wide overbarrier resonances were again got, except that corresponding to $j = 3$ which is supported by the barrier, i.e., it is an orbiting resonance. This narrow resonance appears when the effective potential has no bound levels. Its width is of the same order of magnitude as some orbiting resonances recently reported by Hutson and Le Roy¹¹ using also an approximate, but very precise, method.

As regards Ar-H₂, only overbarrier resonances were found in the range of j values considered. Their widths increase as j increases, obtaining the contrary behavior to that of rotational predissociating levels. So, the higher kinetic energy associated to the resonance, the quicker the system breaks. However, a narrow resonance appears at $j = 2$ despite its character. In order to check our diabatic plus single channel approach for this level, we have carried out close coupling calculations including two open channels ($j = 0, 2$) and a closed one ($j = 4$). We get in this way the same energy position with an error of 0.001 cm^{-1} and a width of 0.82 cm^{-1} . As far as we know, such narrow overbarrier resonances for triatomic X...BC van der Waals systems have not been reported.

To finish, it has seemed to us interesting to reproduce some molecular beam scattering data of orbiting resonance for Ar-H₂.⁵ This constitutes a good test for determining the reliability of the TT potential surface. In particular, we have focused our attention on the resonances labeled by $j = 0; 1 = 8, 9$ in that work.⁵ In our frame, they correspond to $j = 8, 9$, respectively, with $J = 0$, neglecting (artificially) the anisotropic term V_2 . In this way we achieve the kinetic energy values $E(1 = 8) = 14.53 \text{ cm}^{-1}$ and $E(1 = 9) = 22.81 \text{ cm}^{-1}$, while the experimental values are 13.39 ± 0.48 and $21.78 \pm 1.21 \text{ cm}^{-1}$, respectively. As it was already mentioned for the $j = 2$ predissociating level an overestimate in energy resonances of $\sim 1 \text{ cm}^{-1}$ is also found. In addition, we have obtained the corresponding widths $\Gamma(1 = 8) = 2.02 \text{ cm}^{-1}$ and $\Gamma(1 = 9) = 5.71 \text{ cm}^{-1}$. Although we do not dis-

TABLE II. Energies and half-widths (units are cm^{-1}) for Ne-H₂ and Ar-H₂ of bound and metastable predissociating levels. They were obtained by numerical application of the diabatic rotational model with the potentials of Tang and Toennies. A rotational diatomic constant of 56.897 cm^{-1} was assumed.

| j | Ne-H ₂ | | Ar-H ₂ | |
|-----|-------------------|------------------------|-------------------|------------------------|
| | Energy | Half-width | Energy | Half-width |
| 0 | -5.31 | ... | -21.37 | ... |
| 1 | 109.35 | ... | -0.35 | ... |
| | | | 92.26 | ... |
| 2 | 339.14 | 0.102×10^{-1} | 113.68 | ... |
| | | | 322.44 | 0.134×10^{-1} |
| 3 | | | 667.17 | 0.287×10^{-2} |
| 4 | | | 1126.69 | 0.650×10^{-3} |
| 5 | | | 1700.96 | 0.151×10^{-3} |

pose of the experimental widths, a qualitative agreement is found if we examine Fig. 11 of Ref. 5. These results also agree with CC calculations,²⁴ see Fig. 2 in that work, where $\Gamma(9)$ appears to be larger than $\Gamma(8)$ by a factor of ~ 3 .

Finally, we want to stress the long lived shape resonances found for $Ne-H_2$ ($j = 3$) and $Ar-H_2$ ($j = 2$). In principle, they should be amenable to spectroscopic as well as very low energy scattering experiments, providing additional valuable information about the van der Waals interactions. Also, in regard to the method developed here, we conclude that it constitutes a very quick and accurate way to obtain energy positions and widths of all levels (rotational predissociating levels and shape resonances). This procedure may be applied to systems presenting large rotational spacings in the diatomic subunit and low anisotropy. However, the method may be improved, with a little additional computational effort, by introducing discrete-discrete and continuum-continuum couplings, allowing the study of more general systems. Work in this direction is now in progress.

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