

# Spooky correlations and unusual van der Waals forces between gapless and near-gapless molecules

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We consider the zero-temperature van der Waals (vdW) interaction between two molecules, each of which has a zero or near-zero electronic gap between a ground state and the first excited state, using a toy model molecule (equilateral  $H_3$ ) as an example. We show that the van der Waals energy between two ground state molecules falls off as  $D^{-3}$  instead of the usual  $D^{-6}$  dependence, when the molecules are separated by distance  $D$ . We show that this is caused by a perfect “spooky” correlation between the two fluctuating electric dipoles. The phenomenon is related to, but not the same as, the “resonant” interaction between an electronically excited and a ground state molecule introduced by Eisenschitz and London in 1930. It is also an example of “type C van der Waals non-additivity” recently introduced by one of us [J. F. Dobson, *Int. J. Quantum Chem.* **114**, 1157 (2014)]. Our toy molecule  $H_3$  is not stable, but symmetry considerations suggest that a similar vdW phenomenon may be observable, despite Jahn-Teller effects, in molecules with a discrete rotational symmetry and broken inversion symmetry, such as certain metal atom clusters. The motion of the nuclei will need to be included for a definitive analysis of such cases, however. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4967959>]

## I. INTRODUCTION

It is well known that a pair of molecules “ $a$ ” and “ $b$ ” in their dimer ground state experience an attractive dispersion (van der Waals (vdW)) interaction at non-overlapping separations  $D$ . The dispersion interaction comes from coupled quantum-fluctuating multipoles. For  $D$  much greater than the molecular sizes, the dipolar  $D^{-6}$  interaction term dominates and is given by 2nd order perturbation theory as

$$E^{(2)} = - \sum_{J,K} \frac{|\langle 0_a 0_b | \frac{e^2}{D^3} (\vec{X}_a \cdot \vec{X}_b - 3 (\hat{D} \cdot \vec{X}_a) (\hat{D} \cdot \vec{X}_b)) | J_a K_b \rangle|^2}{(E_{J_a} - E_{0_a}) + (E_{K_b} - E_{0_b})} = -C_6^{ab} D^{-6}. \quad (1)$$

Here  $|0\rangle_a$  and  $E_{0_a}$  are the many-electron ground state and energy of molecule  $a$ , respectively, and  $-|e| \vec{X}_a = -|e| \sum_i \vec{r}_{ia}$  is the dipole operator for molecule  $a$ , in which the electronic position operator  $\vec{r}_{ia}$  of electron number  $i$  in molecule  $a$  is measured from the centre of charge of the constituent nuclei.  $|J_a\rangle$  and  $E_{J_a}$  are many-electron eigenfunctions and eigenvalues of molecule  $a$  in isolation, and  $|K_b\rangle$  and  $E_{K_b}$  are those of molecule  $b$  in isolation.  $\hat{D} = \vec{D}/D$  is a unit vector pointing between the molecules.

Eq. (1) is no longer valid if the separation  $D$  is so large that the time  $\tau_{em} = D/c$  for electromagnetic wave propagation between the molecules exceeds a typical correlation time  $\tau_{el}$  of the intramolecular dipolar fluctuations.

There is also clearly a problem with Eq. (1) if both molecules have degenerate electronic ground states so that there exist many-electron states  $|J\rangle_a$  and  $|K\rangle_b$  such that  $E_{J_a} = E_{0_a}$  and  $E_{K_b} = E_{0_b}$ . Then, provided that the relevant dipole matrix element in (1) is nonzero, a discrete term in (1) has a zero denominator leading to a dispersion interaction that does not fall off as  $D^{-6}$  (i.e.,  $C_6^{ab} \rightarrow \infty$ ). Here we will discuss the consequences of this degenerate situation, starting from the (unrealistic) toy model of the  $H_3$  molecule in which the nuclei are constrained to lie on an equilateral triangle. We will then move on to the possibilities for observation of similar anomalous vdW interactions between molecules in other constrained geometries. Finally we will discuss the prospects for observation of such unconventional dispersion forces between real cluster molecules where Jahn-Teller physics and nuclear motion (pseudo-rotation<sup>1,2</sup>) are probably significant.

In such degenerate situations we show below that there are “spooky” correlations between the fluctuating dipoles on the molecules, correlations that do not decay with separation  $D$ , and as a result the dispersion interaction falls off as  $-D^{-3}$  rather than the conventional  $-D^{-6}$ .

In fact similar unusual van der Waals interactions, falling off with an unconventional power of separation, have previously been predicted between extended, low-dimensional nanostructures with a zero HOMO-LUMO gap. Specifically, for two parallel two-dimensional electron gases separated by distance  $Z$ , a sum of  $D^{-6}$  atom–atom contributions

predicts a vdW interaction  $Z^{-4}$  whereas the microscopic theory gives  $Z^{-5/2}$ .<sup>3</sup> For parallel undoped graphene sheets, the conventional summed result is  $E(Z) \propto -Z^{-4}$  whereas microscopic theory gives  $E(Z) \propto -Z^{-3}$  or a logarithmically corrected version of this.<sup>4,5</sup> For the one-dimensional case of two parallel metallic nanotubes at separation  $Z$ , the conventional summed result is  $E(Z) \propto -Z^{-5}$  whereas more accurate microscopic approaches yield  $E(Z) \propto -Z^{-2}(\ln |z|)^{-3/2}$ .<sup>4,6-8</sup> in the electromagnetically non-retarded regime. These 2D and 1D nanosystems were argued<sup>4,9-11</sup> to exhibit unconventional vdW powers because of their zero electronic energy gap and their low dimensionality (limiting the influence of Coulomb screening). In a recent work,<sup>9</sup> these unconventional dispersion power laws were attributed to “Type-C vdW non-additivity” arising from the de-localization (hopping) of electrons between nuclear centres, i.e., to number fluctuations on each centre.

To explain the last statement, it is useful here to summarize the three types of non-pairwise additivity introduced in Ref. 9:

### A. Type A (atomic environment effect)

The dispersion interaction between a single pair of atoms can be expressed in terms of their electric polarizabilities.<sup>12,13</sup> Type-A non-additivity arises from the changes in the polarizability of an atom because of its confinement inside a molecule or other structure, arising, for example, from the compression due to Pauli repulsion from neighboring atoms. This means that one cannot simply use the gas-phase (free-atom) polarizability when computing the vdW energy contribution of any pair of atoms that is a part of larger structures. All of the modern efficient atom-based vdW formalisms (e.g., Refs. 14 and 15) allow for this type-A effect.

### B. Type B (Coulomb screening by spectator atoms)

In the dispersion interaction between two atoms, an electric field couples the electric fluctuations on each atom to those of the other, causing correlations between these fluctuations, correlations whose energy is the dispersion energy. These intermediary electric fields can be changed (screened) when they polarize additional atoms, which produce additional induced fields that affect the original two atoms. This results in an interaction between a collection of more than two atoms, an interaction that is not expressible as a sum over individual pairs of atoms. This type-B effect is missing in the original pairwise atom-based versions of both the popular Grimme<sup>15</sup> and Tkatchenko-Scheffler<sup>14</sup> approaches to the dispersion energy. It is, however, partially included (up to the three-atom Axilrod-Teller-Muto term) in the Grimme DFT-D3 approach.<sup>16,17</sup> The type-B effects are rather completely described in the “many-body dispersion” (MBD) method of Tkatchenko and co-workers.<sup>18</sup> In this approach each atom is treated as a harmonic oscillator, and the Coulomb interactions between atoms are linearized, resulting in an exactly soluble model whose correlation energy is the sum of zero-point energies of collective modes. Apart from its harmonic-atom approximation, the Tkatchenko approach is closely related to the random phase approximation correlation energy, which

can also be written as a sum of zero-point mode energies.<sup>19</sup> Significant qualitative effects of this type-B physics include a dependence of the asymptotic vdW energy  $E$  on the number  $N$  of atoms that is different from the  $E \propto N^2$  dependence predicted by summing pairs of atoms.<sup>20-23</sup> (The last two cited papers used a jellium model for fullerenes and may therefore have included some type-C effects: see the next paragraph. Possibly for this reason, the  $N$ -dependence is slightly different from that in the previous two citations.) Type-B physics also causes quantitative differences from pairwise predictions at all separations, especially for a highly polarizable matter.<sup>20</sup>

### C. Type C (electron hopping/tunneling/number fluctuation effect)

In this scenario, large fluctuating electrical moments can occur via the movement of electrons between atomic centers, with a consequent contribution to the dispersion interaction. This effect is not possible, for example, in theories<sup>14,15,18</sup> that assign an electron uniquely to one atom or another. The consequences of type-C physics for the dispersion energy  $E$  include exponents  $p$ , in the asymptotic decay  $E \approx -AD^{-p}$  with separation  $D$ , that differ from the value predicted by summing over atom pairs.<sup>4</sup> This type-C physics rarely occurs alone: it can be heavily modified by type-B electric screening of the large electric moments that type-C physics, on its own, would create. In particular, in three-dimensional metals the (type-B) Coulomb screening is complete, and the type-C physics makes no qualitative difference. On the other hand, Coulomb screening is incomplete in lower-dimensional zero-gap systems, and there the type-C effect causes unusual asymptotic vdW power laws. For example, the asymptotic interaction  $E$  between two parallel undoped graphene sheets at a low temperature, separated by distance  $D$ , is predicted by a high-level theory to be of the form  $E \approx -A_3D^{-3}$ ,<sup>4</sup> whereas the prediction of atom-pair summation is of the form  $E \approx -A_4D^{-4}$ . At small separations  $D < 5$  nm the gapless transitions that gave rise to the above unusual asymptotic interaction constitute only a small aspect of the vdW interaction, and type-C effects are not important in graphene at these separations. For two 2-dimensional metals the result is  $E \approx -A_{5/2}D^{-5/2}$ .<sup>3</sup> For two parallel conducting one-dimensional wires, the result of the high-level theory is  $E \approx -A_2D^{-2}(\ln D/D_0)^{-3/2}$  compared with  $E \approx -A_5D^{-5}$  from pairwise atomic summation.<sup>3,4,7</sup> These results suggest that the type-C effects are more significant in a lower dimensionality. From this way of thinking, one expects that there can be very strong type-C effects between two gapless “zero-dimensional” systems, i.e., two small molecules, each with a degenerate ground state. The toy model of the H<sub>3</sub> dimer considered in the present work is a case in point.

An attractive feature of the toy model of the equilateral H<sub>3</sub> molecule discussed below is that one can easily isolate the type-C (electron inter-atom hopping) effects from type-B effects (polarization of electrons on individual atoms). This is simply achieved by a configuration interaction (CI) energy calculation for a pair of interacting H<sub>3</sub> molecules in which the one-electron basis is restricted to one s-state on each hydrogen atom. Then dynamic distortion/polarization of the electronic

charge distribution within one atom is not possible, and fluctuating dipole moments are generated solely via hopping of electrons between  $s$  states on different atoms. Some type-B effects can later be introduced by including  $p$  states in the basis, since a superposition of an  $s$  and a  $p$  state exhibits polarization of the electronic cloud on a given H atom. This is done in Sec. V A below.

## II. A TOY MODEL OF SPOOKY DIPOLAR INTERACTIONS: EQUILATERAL $H_3$

To observe the spooky dipolar correlations and  $-D^{-3}$  interaction in the electronic ground state of a molecular pair as proposed above, the discussion following Eq. (1) suggests that one needs to find a molecule with two strictly degenerate ground states that are coupled by the electric dipole operator. Such molecules are not easy to find. The idealized case of a strictly equilateral  $H_3$  molecule is one such case, as we show below. However, a literature search suggests that the  $H_3$  molecule is not stable in its electronic ground state, and a previous work found that the theoretical  $H_3$  conformation of minimum electronic ground state energy would be a linear geometry, not a triangle. In general, even where a candidate degenerate molecule for these effects is stable, one can expect a Jahn-Teller effect to occur, whereby a fully isolated molecule will distort geometrically. We discuss these effects later on in this paper. For now we artificially hold the protons in the equilateral triangle conformation. The toy model that then results is very informative for present purposes. We can adjust the distance between the protons within a molecule in order to explore regimes of weak and strong orbital overlap.

### A. Minimal-basis, independent-electron model of a single equilateral $H_3$

We first study the simplest possible version capable of electronic dipolar excitations, namely, three independent electrons moving in the Coulomb potential due to the nuclei, with a basis consisting of only a single  $s$  state on each nucleus. Thus a distortion of the charge cloud on each nucleus is not possible, and the dipolar fluctuations that lead to the dispersion interaction between two such idealized molecules arise from hopping of the electrons between the localized  $s$  states on the different protons of one molecule (this will lead to the pure “type-C non-additivity” phenomenon in dispersion interactions between such molecules, as proposed in Ref. 9). We first show that this non-interacting three-electron model for a single  $H_3$  molecule has 2 exactly degenerate electronic ground states for each allowed spin configuration. For each spin configuration we further show that the two ground states are coupled by the dipole moment operator. We will then use a limited configuration interaction approach to a pair of  $H_3$  molecules, leading to the spooky  $-D^{-3}$  interaction as described in general above. In Sec. V we will then show, by symmetry arguments and limited CI calculations, that these conclusions survive even when electron–electron interactions are re-introduced and a larger basis is used. In Sec. V A we confirm these conclusions via a larger CI calculation using the package MOLPRO.

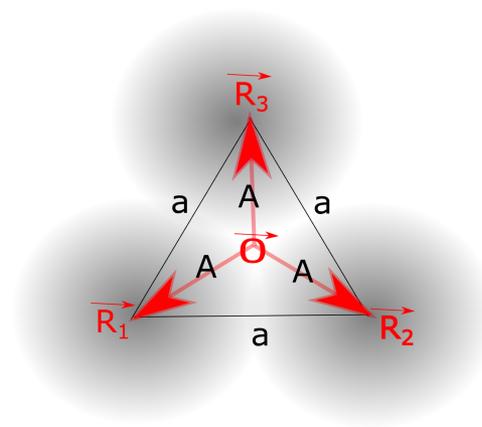


FIG. 1. Geometry of equilateral  $H_3$ .

We label the three protons  $i = 1, 2, 3$  (see Fig. 1). The 6 localized 1-electron  $s$  states are denoted  $|i \uparrow\rangle, |i \downarrow\rangle$  in Dirac notation. The 1-electron Hamiltonian for a spin-up electron is of the form

$$H_{\uparrow}^{1\text{electron}} = \begin{pmatrix} \varepsilon & -t & -t \\ -t & \varepsilon & -t \\ -t & -t & \varepsilon \end{pmatrix}, \quad (2)$$

where  $\varepsilon$  is the 1s energy and  $t$  is a “hopping” matrix element of the hamiltonian between any two sites.  $t$  is usually positive except possibly when the internuclear distance is chosen to be extremely small. The matrix element of the position operator  $\vec{r}$  is as follows:

$$\langle i \uparrow | \vec{r} | j \uparrow \rangle = \begin{cases} (\vec{R}_i + \vec{R}_j) \alpha/2, & i \neq j, \\ \vec{R}_i, & i = j, \end{cases} \quad (3)$$

where  $\vec{R}_i$  is the location of the  $i$ th proton (see Fig. 1 for molecular geometry and labelling). The neighbor overlap element  $\alpha$  in (3) is real and is the same for all neighbor pairs, by symmetry.

We consider the spin-up case for definiteness. A convenient, normalized, maximally symmetric set of 1-electron eigenfunctions of (2) consists of the three Bloch states,

$$\begin{aligned} |g \uparrow\rangle &= \frac{1}{\sqrt{3(1+2\alpha)}} (|1 \uparrow\rangle + |2 \uparrow\rangle + |3 \uparrow\rangle), \\ \varepsilon_{g\uparrow} &= \varepsilon - 2t, \\ |+\uparrow\rangle &= \frac{1}{\sqrt{3(1-\alpha)}} (e^{-i2\pi/3} |1 \uparrow\rangle + e^{-i4\pi/3} |2 \uparrow\rangle + |3 \uparrow\rangle), \\ \varepsilon_{+\uparrow} &= \varepsilon + t, \\ |-\uparrow\rangle &= \frac{1}{\sqrt{3(1-\alpha)}} (e^{+i2\pi/3} |1 \uparrow\rangle + e^{+i4\pi/3} |2 \uparrow\rangle + |3 \uparrow\rangle), \\ \varepsilon_{-\uparrow} &= \varepsilon + t, \end{aligned} \quad (4)$$

where normalization has been ensured by introducing the overlap matrix elements,

$$\langle 1 \uparrow | 1 \uparrow \rangle = 1, \quad \alpha = \langle 1 \uparrow | 2 \uparrow \rangle.$$

The states  $|+\uparrow\rangle, |-\uparrow\rangle$  describe an electron circulating (hopping) clockwise or anti-clockwise around the triangular molecule, respectively. The three Bloch states are eigenfunctions of the  $120^\circ$  rotation operator  $\hat{R}_{120}$ , with eigenvalues 1,  $e^{i2\pi/3}$  and  $e^{-i2\pi/3}$ , respectively. The + and – states

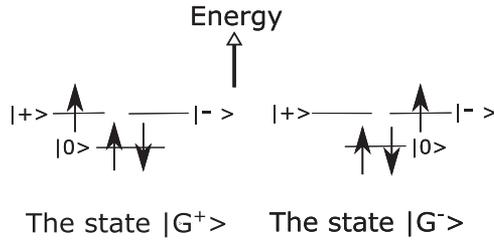


FIG. 2. Two degenerate independent-electron ground states based on clockwise and anticlockwise Bloch orbitals.

are related by the time reversal operation  $\hat{T}$  (complex conjugation with spin not included):  $|-\uparrow\rangle = \hat{T}|+\uparrow\rangle$ . Note that the Hamiltonian commutes with  $\hat{\mathcal{R}}_{120}$  and  $\hat{T}$ , a property which will survive in the more sophisticated interacting models of  $H_3$  to be discussed below. The three Bloch states span the one-body space in the present limited basis.

The matrix elements of the electron position operator  $\vec{r}$  between the Bloch states are from Eqs. (3) and (4)

$$\langle +|\vec{r}|-\rangle = -\frac{1}{2}A(i\hat{x} - \hat{y}) = \langle -|\vec{r}|+\rangle^*, \quad (5)$$

$$\langle +|\vec{r}|+\rangle = \langle -|\vec{r}|-\rangle = \langle g|\vec{r}|g\rangle = \vec{0}, \quad (6)$$

provided that  $\vec{r}$  is measured from the centroid of the proton triangle. Here  $A$  is the distance of each proton from the centroid of the triangle, so that the proton-proton distance is  $a = \sqrt{3}A$  (see Fig. 1).

Two independent, exactly degenerate 3-electron determinantal ground states  $|G^+\rangle$  and  $|G^-\rangle$  each with total spin projection  $+\hbar/2$  are made by doubly occupying ( $\uparrow, \downarrow$ ) the zero Bloch state  $g$  while occupying either the  $+$  or  $-$  Bloch state with an  $\uparrow$  electron,

$$|G^+\rangle = \hat{c}_{g\uparrow}^\dagger \hat{c}_{g\downarrow}^\dagger \hat{c}_{+\uparrow}^\dagger |0\rangle, \quad |G^-\rangle = \hat{c}_{g\uparrow}^\dagger \hat{c}_{g\downarrow}^\dagger \hat{c}_{-\uparrow}^\dagger |0\rangle, \quad (7)$$

where the repeated creation operators  $\hat{c}$ , acting on the vacuum  $|0\rangle$ , generate determinantal states formed from one-electron Bloch orbitals such as  $\phi_{+\uparrow}(\vec{r}) = \langle \vec{r}|+\uparrow\rangle$ , with the correct Fermionic antisymmetry. See Fig. 2.

### III. EQUILATERAL $H_3$ - $H_3$ INTERACTION

We consider two  $H_3$  molecules labelled “a” and “b.” For simplicity we restrict attention to the “facing directly opposite” geometry where the centroids of the molecules are separated by the displacement  $\vec{D} = D\hat{z}$ , and the plane of each molecule is parallel to the  $xy$  plane, with the protons aligned. Then the dipolar inter-molecular coupling Hamiltonian (see Eq. (1)) simplifies to

$$\delta H_{ab} = e^2 D^{-3} \vec{X}_a \cdot \vec{X}_b, \quad \vec{X}_a = \sum_{i=1}^3 \vec{r}_{ia}, \quad (8)$$

where  $\vec{X}_a$  is the total position operator for the electrons in molecule  $a$ . We evaluate the energy of the 6-electron, two-molecule system in a limited configuration interaction approach, keeping only the two degenerate 3-electron ground states on each molecule, leading to a fourfold product-basis set

$$|G^+\rangle_a |G^+\rangle_b, \quad |G^+\rangle_a |G^-\rangle_b, \quad |G^-\rangle_a |G^+\rangle_b, \quad |G^-\rangle_a |G^-\rangle_b \quad (9)$$

or more compactly  $|++\rangle, |+-\rangle, |-+\rangle, |--\rangle$

The intermolecular coupling matrix elements are

$$\begin{aligned} \langle ++|\delta H_{ab}|--\rangle &= \frac{e^2}{D^3} \langle G_a^+ G_b^+ | \vec{X}_a \cdot \vec{X}_b | G_a^- G_b^- \rangle \\ &= \frac{e^2}{D^3} (\langle +|x|-\rangle_a \langle +|x'|-\rangle_b \\ &\quad + \langle +|y|-\rangle_a \langle +|y'|-\rangle_b) \\ &= \frac{e^2}{D^3} \left[ \frac{-1}{2} A(i\hat{x} - \hat{y})_x \frac{-1}{2} A(i\hat{x} - \hat{y})_x \right] \\ &\quad + \frac{e^2}{D^3} \left[ \frac{-1}{2} A(i\hat{x} - \hat{y})_y \frac{-1}{2} A(i\hat{x} - \hat{y})_y \right] \\ &= \frac{e^2}{4D^3} (-A^2) + \frac{e^2}{4D^3} (A^2) = 0. \end{aligned}$$

The vanishing of this matrix element can be understood because the two-molecule states  $|G_a^+ G_b^+\rangle$  and  $|G_a^- G_b^-\rangle$  have different eigenvalues of the total (discrete) angular momentum variable  $\mathcal{L}_{120}$  that generates the (discrete) rotation operators  $1, \mathcal{R}_{120}, \mathcal{R}_{120}^2$ , whereas the scalar operator  $\vec{X}_1 \cdot \vec{X}_2$  is fully rotationally invariant and so conserves  $\mathcal{L}_{120}$ .

The diagonal elements are also zero,  $\langle ++|\delta H_{ab}|++\rangle = \langle --|\delta H_{ab}|--\rangle = \langle +-|\delta H_{ab}|+-\rangle = \langle -+|\delta H_{ab}|-+\rangle$ , but the following cross term is nonzero:

$$\begin{aligned} \langle +-|\delta H_{ab}|-+\rangle &= \frac{e^2}{D^3} \langle G_1^+ G_2^- | \vec{X}_1 \cdot \vec{X}_2 | G^- G^+ \rangle \\ &= \frac{e^2}{D^3} (\langle +|x|-\rangle_1 \langle -|x'|+\rangle_2 \\ &\quad + \langle +|y|-\rangle_1 \langle -|y'|+\rangle_2) \\ &= \frac{e^2}{D^3} \left[ \frac{-1}{2} A(i\hat{x} - \hat{y})_x \frac{-1}{2} A(i\hat{x} - \hat{y})_x^* \right] \\ &\quad + \frac{e^2}{D^3} \left[ \frac{-1}{2} A(i\hat{x} - \hat{y})_y \frac{-1}{2} A(i\hat{x} - \hat{y})_y^* \right] \\ &= \frac{e^2}{4D^3} A^2 + \frac{e^2}{4D^3} A^2 = \frac{e^2 A^2}{2D^3}. \quad (10) \end{aligned}$$

We measure energies relative the ground state energy of two independent  $H_3$  molecules and the CI Hamiltonian then becomes extremely simple (with the states ordered as in Eq. (9)),

$$\hat{H}_{ab} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & \mu D^{-3} & 0 \\ 0 & \mu^* D^{-3} & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad \mu = e^2 A^2 / 2. \quad (11)$$

Two independent bi-molecular states diagonalizing this Hamiltonian are

$$\begin{aligned} |\Phi_e\rangle &= \frac{1}{\sqrt{2}} (|+-\rangle - |-+\rangle), \quad E_e = -\frac{e^2 A^2}{2D^3}, \\ |\Phi_f\rangle &= \frac{1}{\sqrt{2}} (|+-\rangle + |-+\rangle), \quad E_f = +\frac{e^2 A^2}{2D^3}. \end{aligned} \quad (12)$$

The state  $|\Phi_e\rangle$  is the ground state of the  $H_3$ - $H_3$  system and its energy  $-e^2 A^2 / (2D^3)$  falls off with separation  $D$  as  $D^{-3}$  instead of the usual dispersion (vdW) energy, which varies as  $D^{-6}$ . This, with generalization to interacting electrons and a

larger single-electron basis as discussed below, is a principal result of the present work.

#### IV. UNDERSTANDING THE SPOOKY STATE OF THE EQUILATERAL $H_3$ DIMER AS A PAIR OF FLUCTUATING BUT PERFECTLY CORRELATED ELECTRIC DIPOLES

The correlated state (12) is more easily understood by re-expressing it in terms of real 1-electron orbitals  $|up\rangle$ ,  $|down\rangle$  with finite dipole moments, orbitals that are less symmetric than the clockwise and anticlockwise Bloch orbitals  $|+\rangle$ ,  $|-\rangle$  introduced in Eq. (4). We make the (non-unique) choice

$$|up\rangle = \frac{1}{\sqrt{2}}(|+\rangle + |-\rangle), \quad |down\rangle = \frac{1}{\sqrt{2}}(|+\rangle - |-\rangle).$$

The 1-electron charge densities from these two states have dipole moments,

$$\pm \frac{1}{2} |e|A / (1 - \alpha), \quad (13)$$

pointing towards and away from nucleus # 3 of the  $H_3$  triangle, respectively. In the 3-electron ground state manifold of  $H_3$ , the doubly occupied lowest-lying orbital  $|g\rangle$  contributes no electric dipole moment and so we can generate 2 alternative 3-electron ground states  $|G^{up}\rangle$ ,  $|G^{down}\rangle$  with the same dipole moments as in Eq. (13),

$$|G^{up}\rangle = \frac{1}{\sqrt{2}}(|G^+\rangle + |G^-\rangle) = \hat{c}_{g\uparrow}^\dagger \hat{c}_{g\downarrow}^\dagger \hat{c}_{up\uparrow}^\dagger |0\rangle, \quad (14)$$

$$|G^{down}\rangle = \frac{1}{\sqrt{2}}(|G^+\rangle - |G^-\rangle) = \hat{c}_{g\uparrow}^\dagger \hat{c}_{g\downarrow}^\dagger \hat{c}_{down\uparrow}^\dagger |0\rangle, \quad (15)$$

$$\therefore |G^\pm\rangle = \frac{1}{\sqrt{2}}(|G^{up}\rangle \pm i |G^{down}\rangle). \quad (16)$$

We can use (16) to write the correlated ground state from (12) in the form

$$|\Phi_e\rangle = i(|G^{up}\rangle_a |G^{down}\rangle_b - |G^{down}\rangle_a |G^{up}\rangle_b). \quad (17)$$

This exhibits  $|\Phi_e\rangle$  as a state with perfect anticorrelation between the electric dipole moments on the two  $H_3$  molecules: when one is “up” the other is “down,” and vice versa. This perfect correlation does not decay with intermolecular distance  $D$ , since the coefficients  $\pm i$  in the superposition (17) are  $D$ -independent. This means that, although the  $D^{-3}$  decay of the vdW interaction here is same as for two fixed dipoles, this is different from that case because the interaction can be repulsive for fixed dipoles depending on orientation, whereas the present effect is always attractive in the dimer ground state. It is a true van der Waals interaction. It can also be compared with the non-decaying “spooky” correlations between spins or between photons in the study of quantum computing situations. The difference here is that the correlated entities are electric dipoles rather than electron spins or photons.

It is also instructive, for later use, to write the two-molecule CI Hamiltonian in the following basis of electric dipole states:

$$|G^{up}\rangle_a |G^{up}\rangle_b, \quad |G^{up}\rangle_a |G^{down}\rangle_b, \quad |G^{down}\rangle_a |G^{up}\rangle_b, \\ |G^{down}\rangle_a |G^{down}\rangle_b$$

giving

$$H'_{ab} = \begin{pmatrix} \frac{1}{2} \frac{\mu}{D^3} & 0 & 0 & \frac{1}{2} \frac{\mu}{D^3} \\ 0 & -\frac{1}{2} \frac{\mu}{D^3} & \frac{1}{2} \frac{\mu}{D^3} & 0 \\ 0 & \frac{1}{2} \frac{\mu}{D^3} & -\frac{1}{2} \frac{\mu}{D^3} & 0 \\ \frac{1}{2} \frac{\mu}{D^3} & 0 & 0 & \frac{1}{2} \frac{\mu}{D^3} \end{pmatrix}, \quad (18)$$

where  $\mu = e^2 A^2 / 2$ . The Hamiltonian matrix (18) naturally has the same eigenvalues  $0, 0, -\frac{\mu}{D^3}, \frac{\mu}{D^3}$  as the original matrix (11) that used the  $+, -$  basis.

Our analysis above is quite consistent with the treatment of “quantum electrical dipoles” given by Allen, Abanov, and Requist.<sup>24</sup>

#### V. MINIMAL-BASIS ANALYSIS OF 3-ELECTRON STATES IN $H_3$ INCLUDING ON-SITE REPULSION

When the electron–electron interaction is included in the model of a single equilateral  $H_3$ , the interacting Hamiltonian still has an invariance under the  $120^\circ$  rotation operator  $\mathcal{R}_{120}$  and also under time reversal  $\hat{T}$ . Therefore, just as for the independent-electron model above, we expect that there will be a degenerate pair of 3-electron states  $|G^+\rangle$  and  $|G^-\rangle$  that are analogous to non-interacting states defined in Eq. (7). In particular they differ by a time reversal and are eigenfunctions  $\mathcal{R}_{120}$  with eigenvalues  $\exp(\pm i2\pi/3)$  (note that, since  $\mathcal{R}_{120}^3 = 1$ , the only possible eigenvalues of  $\mathcal{R}_{120}$  are the three complex cube roots of 1). The matrix element  $\langle G_a^+ G_b^+ | \vec{X}_a \cdot \vec{X}_b | G_a^- G_b^- \rangle$  will therefore still be zero by the symmetry argument given above, and we expect that  $\langle G_a^+ G_b^- | \vec{X}_a \cdot \vec{X}_b | G_a^- G_b^+ \rangle$  will still be non-zero. The question is whether these two degenerate states are still ground states. We have set up a  $9 \times 9$  spin-restricted Hamiltonian matrix including an on-site repulsion energy  $U$  as well as hopping elements  $-t$ . At fixed on-site repulsion  $U$ , we find that two time-reversed degenerate states  $|G^+\rangle$  and  $|G^-\rangle$  remain the ground states for all positive  $t$  except for  $t = 0$  exactly. For  $t = 0$  the three exactly degenerate ground states have no double occupation of any proton site. We also verified explicitly that

$$\langle G_a^+ G_b^+ | \vec{X}_a \cdot \vec{X}_b | G_a^- G_b^- \rangle = 0, \quad \langle G_a^+ G_b^- | \vec{X}_a \cdot \vec{X}_b | G_a^- G_b^+ \rangle \neq 0.$$

However, as  $t$  decreases towards zero, the gap from the ground state doublet of each  $H_3$  unit, to the next state, goes towards zero. Thus for small  $t$ , corresponding to a uniformly stretched  $H_3$  triangle, our two-state limited CI analysis of the  $H_3$ – $H_3$  becomes invalid. This means that when seeking real systems that exhibit the unusual vdW interaction (12), it would be best to look at, e.g., clusters of metal atoms that favor hopping of electrons between nuclei, as suggested by the metallic nature of bulk metals.

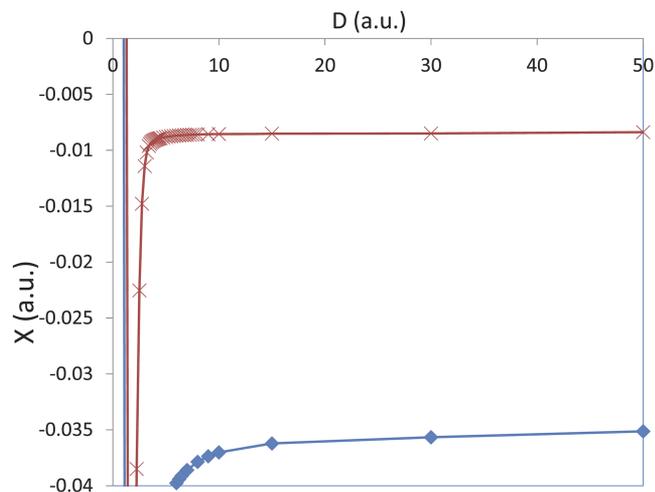


FIG. 3. Results of FCI calculations demonstrating that the interaction energy  $\Delta E$  of two  $H_3$  molecules falls off as  $\Delta E \approx -C_3 D^{-3}$ , both with an s-only basis and with an s + p basis. We plot the quantity  $X = D^3 \Delta E$  vs.  $H_3$ - $H_3$  separation  $D$ .  $X$  will be independent of  $D$  if the  $\Delta E \approx -C_3 D^{-3}$  power law holds. Electron-electron interactions are retained within and between molecules in both cases. Crosses: s basis only. Diamonds: s + p basis.

### A. Larger-basis analysis of interacting 3-electron states in $H_3$

We also performed full CI, limited-basis calculations using MOLPRO, to study the equilateral  $H_3$  dimer system with a larger basis and all the electron-electron interactions, reaching the same qualitative conclusions as above. This calculation allows static and dynamic distortions of the electron density on each proton (type-B nonadditive vdW effect<sup>9</sup>), as well as the previously considered “type-C” effects due to hopping of electrons between the protons. Figure 3 shows the quantity  $D^3 \Delta E$  versus  $H_3$ - $H_3$  separation  $D$ , where  $\Delta E = E(D) - E(\infty)$  is the binding energy of the  $H_3$ - $H_3$  dimer. Results are shown for the T1.2 symmetry, which gives the dimer ground state at all the  $D$  values considered. Two FCI calculations were performed, one with a 1s-only basis and one with p orbitals in the basis as well. In each case the curve becomes flat at larger separations, indicating that  $\Delta E \propto -D^{-3}$  as predicted on symmetry grounds by the above theory.

Interestingly, the  $D^{-3}$  interaction is stronger with the  $p$  orbitals included, suggesting that the dynamic distortions of the charge cloud on each atom (type-B effect<sup>9</sup>) are assisting rather than hindering the type-C (inter-atom hopping) polarizability, in the present geometry.

Elsewhere we plan to present further full CI data for larger bases and also for the near-degenerate Jahn-Teller-distorted (isosceles) cases introduced below.

## VI. STATIC JAHN-TELLER DISTORTIONS

If the nuclear positions of a single isolated molecule are allowed to relax, the exact electronic degeneracy proposed here can lead to an energy-lowering Jahn-Teller distortion,<sup>25</sup> causing broken rotational symmetry of the proton configuration in the ground state. The electronic eigenstates proposed above will then be replaced by non-degenerate states with a dipole moment. This completely changes the situation for  $H_3$ , which

in fact is believed to be unstable in its electronic ground state, and if it were stable, would Jahn-Teller distort continuously to a linear configuration. Thus our example of equilateral  $H_3$  is just a toy model requiring an external agent to hold the nuclear positions fixed. However in cases where the nuclear framework of a candidate cluster molecule is sufficiently rigid, such distortions will be small and will introduce only a small energy gap  $\varepsilon_g$ . Candidate systems for this situation might include transition or rare earth metal clusters where the observed enhanced rigidity of the bulk metal (compared to the simple s-p metals) suggests that directional bonds may provide the needed structural rigidity, while the hopping  $t$  tends to dominate on-site repulsion  $U$  (leading to full metallic behavior in the limit of a large number of atoms). Metal atom clusters are only one possibility, however, and one could envisage many other possibilities for stiff structures with the required symmetry properties, based, for example, on the rigidity of graphene hexagons.

To commence exploration of the effects of the Jahn-Teller phenomenon, we therefore now investigate the simplest model with a static distortion, namely, isosceles  $H_3$  with frozen nuclear positions. We will show that spooky vdW correlations can still occur in a significant subasymptotic regime of separations provided that the distortion-induced energy gap  $\varepsilon_g$  is small enough.

## VII. TRIANGULAR $H_3$ WITH A WEAK ISOSCELES DISTORTION

We consider an isosceles triangle of protons with base  $b$  and height  $h$ , with protons at positions  $\vec{R}_1 = -b\hat{x}/2 - h\hat{y}/3$ ,  $\vec{R}_2 = +b\hat{x}/2 - h\hat{y}/3$ , and  $\vec{R}_3 = \frac{2}{3}h\hat{y}$  (measured relative to the centre of charge  $O$  of the protons, at height  $h/3$  above the base). (See Fig. 4.) Initially we work again in the independent-electron model, with 3 electrons moving between the stationary protons.

The reduction of the hopping matrix elements involving the more distant atom #3 leads to a one-electron Hamiltonian in the minimal localised atomic basis  $|1\rangle, |2\rangle, |3\rangle$ , centered on the protons, as follows:

$$\hat{H} = \varepsilon + \begin{pmatrix} 0 & -t & -t' \\ -t & 0 & -t' \\ -t' & -t' & -\Delta \end{pmatrix}, \quad (19)$$

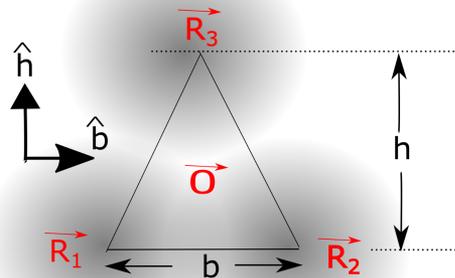


FIG. 4. Geometry of isosceles  $H_3$ .

where  $t'$  is the hopping element to/from the apex, atom #3 (see Fig. 4) and  $\Delta$  is the additional energy of an electron on proton 3 as a result of orbital compression in the ground state. Here for an acute isosceles triangle we expect  $\Delta < 0$  and  $0 < t' < t$  so that  $\delta \equiv t' - t < 0$ . For an obtuse isosceles triangle,  $\Delta > 0$  and  $\delta > 0$ . The eigenvalues of (19) are as follows:

$$\varepsilon^{(1)} = \varepsilon + \frac{1}{2}\Delta - \frac{1}{2}t - \frac{1}{2}\sqrt{(t + \Delta)^2 + 8(t')^2}, \quad (20)$$

$$\varepsilon^{(2)} = \varepsilon + \frac{1}{2}\Delta - \frac{1}{2}t + \frac{1}{2}\sqrt{(t + \Delta)^2 + 8(t')^2}, \quad (21)$$

$$\varepsilon^{(3)} = \varepsilon + t.$$

In the equilateral limit we have  $\Delta = 0$ ,  $t' = t$  and we recover  $\varepsilon^{(1)} = \varepsilon - 2t$ ,  $\varepsilon^{(2)} = \varepsilon + t$ ,  $\varepsilon^{(3)} = \varepsilon + t$  as found earlier for the equilateral case. For an acute isosceles triangle (apical angle  $\theta_3 < 90^\circ$ ,  $|\vec{R}_3 - \vec{R}_1| > |\vec{R}_2 - \vec{R}_1|$ ), state (1) is the one-electron ground orbital and  $\varepsilon^{(3)} > \varepsilon^{(2)} > \varepsilon^{(1)}$ . If the isosceles triangle is only slightly distorted from an equilateral triangle, then  $\Delta$  and  $\delta \equiv t' - t$  are both small. In this region we can Taylor-expand (21) giving an energy gap

$$\varepsilon_{gap} \equiv \varepsilon^{(3)} - \varepsilon^{(2)} = -\frac{5}{6}\Delta - \frac{4}{3}\delta + O(\Delta^2, \delta^2, \Delta\delta) > 0. \quad (22)$$

This will be the gap between the ground and first excited orbital for independent electrons in an acute isosceles  $H_3$  molecule. The lowest three-electron states have the  $\varepsilon^{(1)}$  orbital doubly occupied, and for the acute triangle case the ground state has the  $\varepsilon^{(2)}$  orbital singly occupied. Equally, for an obtuse isosceles  $H_3$  molecule the ground state involves  $\varepsilon^{(3)}$  rather than  $\varepsilon^{(2)}$ , and then (22) is negative, and the gap is  $\varepsilon_g = \varepsilon^{(2)} - \varepsilon^{(3)} \approx \frac{5}{6}\Delta + \frac{4}{3}\delta > 0$ .

The normalized one-electron eigenfunctions of (19) are, with respect to s orbitals on the three protons as basis,

$$\begin{aligned} |v^{(1)}\rangle &= \sqrt{N_1} \left( -\frac{1}{2} \frac{\varepsilon^{(2)} + \Delta - \varepsilon}{t'}, -\frac{1}{2} \frac{\varepsilon^{(2)} + \Delta - \varepsilon}{t'}, 1 \right), \\ |v^{(2)}\rangle &= \sqrt{N_2} \left( -\frac{1}{2} \frac{\varepsilon^{(1)} + \Delta - \varepsilon}{t'}, -\frac{1}{2} \frac{\varepsilon^{(1)} + \Delta - \varepsilon}{t'}, 1 \right), \\ |v^{(3)}\rangle &= \sqrt{N_3}(-1, 1, 0), \end{aligned} \quad (23)$$

where the normalizing factors  $N_i$  depend on the direct overlaps  $\alpha_{23} = \alpha_{13}$ ,  $\alpha_{12}$ . From (23) we find that the one-electron states have large dipole moment vectors  $\vec{d}$  for arbitrarily small isosceles distortions, even though the energy gap (22) is arbitrarily small. Specifically

$$\begin{aligned} \vec{d}_1 &\equiv -|e| \langle v^{(1)} | \vec{r} | v^{(1)} \rangle = \eta_1 \hat{h}, \\ \vec{d}_2 &\equiv -|e| \langle v^{(2)} | \vec{r} | v^{(2)} \rangle = \eta_2 \hat{h}, \\ \vec{d}_3 &\equiv -|e| \langle v^{(3)} | \vec{r} | v^{(3)} \rangle = \eta_3 \hat{h}, \\ \vec{d}_{23} &\equiv -|e| \langle v^{(2)} | \vec{r} | v^{(3)} \rangle = \eta_{23} \hat{b}, \end{aligned} \quad (24)$$

where  $\hat{b}$  is a unit vector pointing from proton 1 to proton 2 along the base of the isosceles triangle, and  $\hat{h}$  is a unit vector perpendicular to  $\hat{b}$  and directed towards the apex

(proton 3); see Fig. 4. For independent electrons the coefficients take the nonzero values

$$\begin{aligned} \eta_1 &= \frac{-|e|N_1}{3} \left( -\frac{1}{2} \left( \frac{\varepsilon^{(2)} + \Delta - \varepsilon}{t'} \right)^2 (1 + \alpha) \right. \\ &\quad \left. + 2 - \frac{1}{2} \frac{\varepsilon^{(2)} + \Delta - \varepsilon}{t'} \alpha_{23} \right) h, \\ \eta_2 &= \frac{-|e|N_2}{3} \left( -\frac{1}{2} \left( \frac{\varepsilon^{(1)} + \Delta - \varepsilon}{t'} \right)^2 (1 + \alpha) \right. \\ &\quad \left. + 2 - \frac{1}{2} \frac{\varepsilon^{(2)} + \Delta - \varepsilon}{t'} \alpha_{23} \right) h, \\ \eta_3 &= \frac{-|e|2N_3(1 - \alpha)}{3} h, \\ \eta_{23} &= -|e| \sqrt{N_2 N_3} \left( -\frac{1}{2} \frac{\varepsilon^{(1)} + \Delta - \varepsilon}{t'} + \frac{1}{2} \alpha_{23} \right) b, \end{aligned}$$

where the  $\{\alpha_{ij}\}$  are overlap matrix elements between neighbouring atomic s functions and the  $\{\sqrt{N_i}\}$  are normalizing factors for eigenfunctions  $|v^{(i)}\rangle$ .

From the one-body states  $|v^{(i)}\rangle$  we construct two low-lying determinantal states  $|B\rangle, |S\rangle$  of three independent electrons in the isosceles  $H_3$  triangle, each with two electron spins up ( $\uparrow$ ) and one down ( $\downarrow$ ) giving total spin angular momentum  $+\hbar/2$ ,

$$|B\rangle = c_{1\uparrow}^\dagger c_{1\downarrow}^\dagger c_{2\uparrow}^\dagger |0\rangle, \quad |S\rangle = c_{1\uparrow}^\dagger c_{1\downarrow}^\dagger c_{3\uparrow}^\dagger |0\rangle.$$

These states are separated by a small gap  $\varepsilon_{gap}$  given by Eq. (22). For the acute isosceles triangle, the state  $|B\rangle$  with an electric dipole moment pointing towards the base (“B”) of the triangle is the ground state, while the state  $|S\rangle$  with a dipole pointing to the apex or summit (“S”) is the ground state for the obtuse case. The dipole matrix elements for a single molecule are as follows:

$$\begin{aligned} \vec{d}_B &\equiv -|e| \langle B | \vec{r}_1 + \vec{r}_2 + \vec{r}_3 | B \rangle = 2\vec{d}_1 + \vec{d}_2 = -|\vec{d}_B| \hat{h}, \\ \vec{d}_S &= -|e| \langle U | \vec{r}_1 + \vec{r}_2 + \vec{r}_3 | U \rangle = 2\vec{d}_1 + \vec{d}_3 = |\vec{d}_S| \hat{h}, \\ \vec{d}_{BS} &\equiv -|e| \langle B | \vec{r}_1 + \vec{r}_2 + \vec{r}_3 | S \rangle = \vec{d}_{SB} = |\vec{d}_{UD}| \hat{b}. \end{aligned} \quad (25)$$

The vector directions (parallel to  $\hat{h}$  or  $\hat{b}$ ) of these matrix elements stem from the mirror symmetry of the isosceles triangle and remain valid when we introduce the electron-electron interaction, thereby going beyond our initial neglect of electron-electron interactions inside the  $H_3$  triangle.

### A. Two parallel facing isosceles $H_3$ units, $H_3a$ , and $H_3b$

For small enough gap  $\varepsilon_g$ , we need to only keep, as our two-molecule product basis, the ground state and lowest 3 excited noninteracting states of the  $H_3$ - $H_3$  complex, namely,  $|S\rangle_a |S\rangle_b$ ,  $|S\rangle_a |B\rangle_b$ ,  $|B\rangle_a |S\rangle_b$ ,  $|B\rangle_a |B\rangle_b$  in that order. In this basis the bi-molecular Hamiltonian matrix (relative to two isolated ground state molecules), including the dipole interaction  $\delta H = e^2 X_a X_b / D^3$  between the

molecules, is

$$H_{ab} = \begin{pmatrix} 2\varepsilon_g + cD^{-3} & 0 & 0 & gD^{-3} \\ 0 & \varepsilon_g + \beta D^{-3} & fD^{-3} & 0 \\ 0 & fD^{-3} & \varepsilon_g + \beta D^{-3} & 0 \\ gD^{-3} & 0 & 0 & aD^{-3} \end{pmatrix}, \quad (26)$$

where

$$a = |\vec{d}_B|^2 > 0, \quad \beta = \vec{d}_B \cdot \vec{d}_S < 0, \quad c = |\vec{d}_S|^2 > 0, \\ f = g = |\vec{d}_{SB}|^2 > 0. \quad (27)$$

The Hamiltonian (26) is very similar to that for the equilateral case in the broken-symmetry “up” “down” 1-electron basis: see Eq. (18). The zeros in the matrix (26) come from matrix elements such as

$$\langle B_a B_a | \vec{R}_a \cdot \vec{R}_b | B_a S_b \rangle = \vec{d}_B \cdot \vec{d}_{BS} = |\vec{d}_B| |\vec{d}_{BS}| \hat{h} \cdot \hat{b} = 0.$$

This zero arises mathematically from the orthogonality of the unit vectors  $\hat{b}$  and  $\hat{h}$  and is mandated physically by the mirror symmetry of the isosceles molecule. This symmetry survives when our original neglect of the intramolecular electron–electron interaction is relaxed. The form of Eq. (26) is therefore valid even with inclusion of electron–electron interactions within each H<sub>3</sub> molecule, though the coefficients  $a, \beta, c, \dots, g$  will be determined by the dipolar matrix elements  $\vec{d}$  with e-e interactions included. As for the equilateral case, however, we expect that if the on-site e-e repulsion  $U$  is too strong compared with the hopping amplitude  $t$ , the states  $|B\rangle$  and  $|S\rangle$  may no longer be well-separated energetically from the next excited state of the H<sub>3</sub> molecule, invalidating the present analysis.

It is easily shown that in the limits  $\Delta \rightarrow 0$ ,  $t' \rightarrow t$ , corresponding to the equilateral limit of isosceles triangles (26) reduces to (18).

The eigenenergies of the interacting isosceles H<sub>3</sub>–H<sub>3</sub> system (measured from the ground state of two isolated H<sub>3</sub> units) from diagonalization of (26), are as follows:

$$E_{IV} = \frac{1}{2D^3} \left( c + a + 2\varepsilon_g D^3 + \sqrt{(c - a + 2\varepsilon_g D^3)^2 + 4g^2} \right), \quad (28)$$

$$E_{III} = \frac{1}{2D^3} \left( c + a + 2\varepsilon_g D^3 - \sqrt{(c - a + 2\varepsilon_g D^3)^2 + 4g^2} \right), \quad (29)$$

$$E_{II} = \varepsilon_g + \frac{\beta + f}{D^3}, \quad (30)$$

$$E_I = \varepsilon_g + \frac{\beta - f}{D^3}. \quad (31)$$

## B. Asymptotic regime of isosceles H<sub>3</sub>–H<sub>3</sub> interaction: Conventional fixed dipolar, vdW, and (excited) resonant interactions

Since the (frozen) isosceles distortion away from an equilateral configuration has introduced an energy gap  $\varepsilon_g$  and a large permanent electric dipole  $\vec{d}_B$  in the H<sub>3</sub> ground state, one might initially expect that the ground state H<sub>3</sub>–H<sub>3</sub>

interaction would be a sum of a conventional attractive vdW interaction varying as  $D^{-6}$  plus a fixed-dipolar interaction that varies as  $D^{-3}$  and that can be attractive or repulsive. This is indeed the case in the truly asymptotic regime defined by

$$D > D_{\max} \equiv \left( |\vec{d}_{\max}|^2 / \varepsilon_g \right)^{1/3},$$

where  $|\vec{d}_{\max}|$  is the greatest of the dipole matrix magnitudes from (25). In this regime we can Taylor-expand the eigenenergies (28), (29) giving the following energies,  $E_{III}$ ,  $E_I, E_{II}$ ,  $E_{IV}$ , ordered from the lowest to the highest,

$$E_{III} = aD^{-3} - \frac{g^2}{2\varepsilon_g} D^{-6} + O(D^{-8}). \quad (32)$$

This state III is the ground state of the H<sub>3</sub>–H<sub>3</sub> dimer and exhibits a conventional attractive  $D^{-6}$  vdW interaction plus a repulsive  $D^{-3}$  interaction between the fixed molecular dipoles (repulsive because we have assumed that the two parallel-facing H<sub>3</sub> molecules have the same alignment so that  $a > 0$ ). The next-lowest energies are as follows:

$$E_I = \varepsilon_g + \frac{b - f}{D^3}, \quad E_{II} = \varepsilon_g + \frac{b + f}{D^3}. \quad (33)$$

Since  $\beta < 0$  and  $f > 0$  (see Eq. (27)), state I with energy  $E_I$  is the first excited state of the H<sub>3</sub> dimer. Its energy is just below  $\varepsilon_g$ , corresponding to its origin as a superposition of two product states in each of which just one of the molecules is excited. This is the attractive “resonant interaction” introduced already by Eisenschitz and London in 1930.<sup>26</sup> Such resonant excited states depend on the two gaps having the same nonzero value  $\varepsilon_g$ , and the coupled state is related to the concept of excitons in condensed matter systems. Similar physics is important for understanding intramolecular transport of photon energy in chromophores.<sup>27</sup> State II has a similar physical origin but has a higher energy than  $E_I$  and can give repulsion rather than attraction.

The highest-lying molecular dimer state from (26), labelled IV, has an energy close to twice the gap energy,

$$E_{IV} = 2\varepsilon_g + O(D^{-3}). \quad (34)$$

## C. Subasymptotic regime of spooky $D^{-3}$ vdW interaction between isosceles H<sub>3</sub> molecules

We will now show that if the gap  $\varepsilon_g$  is sufficiently small, there is a significant sub-asymptotic spatial regime where the interaction is always attractive and varies as  $D^{-3}$  just as for the equilateral case treated above. The relevant regime is

$$A < D < D_1 \equiv \left( |d_{\min}|^2 / \varepsilon_g \right)^{1/3}, \quad (35)$$

where  $|d_{\min}|$  is the least magnitude of the dipolar matrix elements (25) and  $A$  is the spatial size of each molecule. In this regime the energies (31)–(28) can be written, with the lowest listed first and the highest listed last,

$$E_I \approx \varepsilon_g + \frac{\beta - f}{D^3} \text{ bimolecular groundstate,} \\ \text{spooky attractive vdW,} \quad (36)$$

$$E_{II} \approx \varepsilon_g + \frac{\beta + f}{D^3} \text{ excited bimolecular state,} \quad (37)$$

$$E_{III} \approx \frac{1}{2D^3} \left( a + c - \sqrt{(a-c)^2 + 4g^2} \right) \text{ excited bimolecular state,} \quad (38)$$

$$E_{IV} \approx 2\varepsilon_g + \frac{1}{2D^3} \left( a + c + \sqrt{(a-c)^2 + 4g^2} \right) > 0 \text{ highest bimolecular state.} \quad (39)$$

In this regime the terms proportional to  $\varepsilon_g$  are small compared with other terms in (36), (37), and (39). By comparing (36) with (33), one learns that the spooky correlated state arises as the small-gap limit of the attractive resonant interaction, but it is now the bimolecular ground state, and not an excited state as in the usual resonant interaction.

This subasymptotic regime does not exist for most molecules because, for example, with a gap  $\varepsilon_g \approx 1$  eV and a dipole moment ( $1 \text{ \AA}$ ) ( $|e|$ ), the outer limit of the subasymptotic spatial regime from (35) is at  $D_1 \approx 2.5 \text{ \AA}$  which lies in the overlap region of electronic clouds where the present approach is not valid. However with a gap of  $\varepsilon_g = 0.01$  eV and the same dipole moment we find  $D_1 \approx 12 \text{ \AA}$  which leaves a viable subasymptotic region. Larger dipole moments and smaller gaps will extend  $D_1$  to larger values.

### VIII. OTHER MOLECULES LIKELY TO HAVE ELECTRONIC DEGENERACY SIMILAR TO $\text{H}_3$

In the working above, the important features of a molecule leading to an anomalous  $D^{-3}$  vdW interaction with another such molecule in the dimer ground state were that an individual molecule has two degenerate electronic ground states that are coupled by the dipole operator. To achieve this in a similar manner to the equilateral  $\text{H}_3$  molecule studied above, we propose that one should consider molecules with the following features:

- (i) Discrete  $N$ -fold rotational symmetry (and an odd number of electrons) leading to two degenerate Bloch-type many-electron states  $\Psi_+$ ,  $\Psi_- = \Psi_+^*$  for each spin configuration, states that are a time-reversed pair (complex conjugates), each of which is an eigenfunction of the rotation operator  $\hat{R}_{360^\circ/N}$ .
- (ii) Sufficiently large ratio  $t/U$  of the hopping amplitude  $t$  to on-site electronic repulsion  $U$  to ensure that the two symmetry-mandated degenerate states are well-separated from higher states, validating our very-small-basis CI treatment.
- (iii) An odd  $N$  value,  $N = 2n + 1$ ,  $n = 1, 2, 3, \dots$ . This is needed because for the even case  $N = 2n$ , one can show that the relevant matrix element of the dipole operator is zero. To prove this, note that for the spooky effect we need a degenerate time-reversed pair of many-electron states  $\Psi_1(\vec{\xi}) \equiv \langle \vec{\xi} | + \rangle$ ,  $\Psi_2(\vec{\xi}) = \langle \vec{\xi} | - \rangle = \Psi_1^*(\vec{\xi})$  that are both eigenstates of the rotation operator  $\hat{R}_{360^\circ/(2n)} = \hat{R}_{180^\circ/n}$ . Here for an  $M$ -electron molecule we have denoted

$$\vec{\xi} = (\vec{r}_1, \vec{r}_2, \dots, \vec{r}_M) = (x_1, y_1, z_1 : x_2, y_2, z_2 : \dots : x_M, y_M, z_M).$$

Since for even-order rotational symmetry  $\Psi_1$  and  $\Psi_2$  are eigenstates of  $\hat{R}_{180^\circ/n}$ , they are also eigenstates of  $(\hat{R}_{180^\circ/n})^n = \hat{R}_{180^\circ}$ ,

$$\hat{R}_{180^\circ} \Psi_1 = \theta_1 \Psi_1, \quad \hat{R}_{180^\circ} \Psi_2 = \theta_1^* \Psi_2. \quad (40)$$

Further since two  $180^\circ$  rotations produce no net effect we have  $(\hat{R}_{180^\circ})^2 = \hat{I}$  and so in (40) we have  $\theta_1^2 = 1 \Rightarrow \theta_1 = 1$  or  $-1$ .

However the  $180^\circ$  rotation operator  $\hat{R}_{180^\circ}$  is in fact the spatial coordinate inversion operator in the plane perpendicular to the rotational symmetry axis,

$$\hat{R}_{180^\circ} \Psi(\vec{\xi}) \equiv \Psi(\vec{\xi}'),$$

where for an  $M$ -electron molecule,

$$\vec{\xi}' = (-x_1, -y_1, z_1 : -x_2, -y_2, z_2 : \dots : -x_M, -y_M, z_M).$$

Then the matrix element of the molecular dipole operator between the two time-reversed states is

$$\begin{aligned} \langle - | \vec{d} | + \rangle &= -|e| \int \Psi_2^*(\vec{\xi}) (\vec{r}_1 + \vec{r}_2 + \dots + \vec{r}_M) \Psi_1(\vec{\xi}) d^3M \xi \\ &= -|e| \int (\Psi_1(\vec{\xi}))^2 (\vec{r}_1 + \vec{r}_2 + \dots + \vec{r}_M) d^3M \xi. \end{aligned}$$

To obtain our spooky inter-molecule correlation for parallel-facing dimer geometry, we need each molecule to exhibit non-zero Cartesian components of the dipole matrix element  $\langle - | \vec{d} | + \rangle$  in the  $xy$  plane perpendicular to the rotational symmetry ( $z$ ) axis. These components form a perpendicular dipole matrix element  $\langle - | \vec{d}_\perp | + \rangle$ ,

$$\begin{aligned} \langle - | \vec{d}_\perp | + \rangle &\equiv d_x \hat{x} + d_y \hat{y} = -|e| \int (\Psi_1(\vec{\xi}))^2 \\ &(\vec{r}_{1\perp} + \vec{r}_{2\perp} + \dots + \vec{r}_{M\perp}) d^3M \xi. \quad (41) \end{aligned}$$

But  $(\Psi_1(\vec{\xi}))^2 = (\theta_1^{-1} \Psi_1(\vec{\xi}'))^2 = \theta_1^{-2} (\Psi_1(\vec{\xi}'))^2 = 1 (\Psi_1(\vec{\xi}'))^2$ . Thus  $\Psi_1^2$  is even under the inversion  $\vec{\xi} \rightarrow \vec{\xi}'$  of  $\vec{r}_{i\perp}$  ( $x_i$  and  $y_i$ ) coordinates so that the integrand of (41) is odd and the integral vanishes.

The conclusion is then that we will not obtain a spooky  $-D^{-3}$  vdW interaction for a system with an even ( $2n$ -fold) rotation symmetry because the implied inversion symmetry makes the needed dipolar coupling vanish. Rather we should look only for molecules with odd rotational symmetry ( $3$ -fold,  $5$ -fold,  $\dots$ ).

A similar argument based on rotational symmetry shows that (for even or odd  $N$ ) the dipole moment in either of the two degenerate states is also zero:  $\langle + | \vec{d}_\perp | + \rangle = \langle - | \vec{d}_\perp | - \rangle = \vec{0}$ : this was the other matrix element needed to ensure that the correlation problem for more general molecules is isomorphic to the  $\text{H}_3$  problem treated above.

Thus to obtain a  $D^{-3}$  vdW interaction in a similar fashion to that obtained for a pair of  $\text{H}_3$  molecules above, we need to search for molecules that have a discrete odd rotational symmetry. Regular  $(2n + 1)$ -gons satisfy this when  $n = 1, 2, 3, \dots$ . So do a large number of cluster structures: for two examples see Fig. 5. Of course, this combination of properties may not be the only way to achieve spooky vdW interactions, but it does suggest one class of molecules to explore.

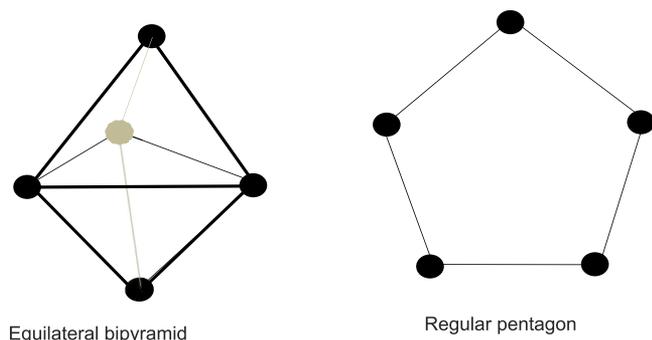


FIG. 5. Two geometries conducive to spooky vdW forces.

Furthermore, our numerical studies of equilateral  $H_3$  showed that the hopping of electrons between sites needs to dominate over on-site Coulomb repulsion in order for the two-fold degenerate ground states to be well separated from the first excited state, as required for the validity of our limited-CI analysis of the inter-molecular interaction. These requirements suggest that clusters of metal atoms might be suitable candidates.

As an example of the importance of breaking inversion symmetry via an odd rotational symmetry, we also studied the square  $H_4$  molecule, which has a discrete ( $90^\circ$ ) rotational symmetry and therefore has an inversion symmetry, unlike equilateral  $H_3$ . We found no anomalous  $D^{-3}$  vdW interaction between two  $H_4$  molecules, though an always-attractive  $D^{-5}$  vdW interaction may be possible via spooky coupled quadrupolar fluctuations. This work will be described elsewhere.

## IX. EFFECTS OF NUCLEAR MOTION—METAL ATOM CLUSTERS

The Jahn-Teller-distorted state of our target molecules should have a permanent electric dipole, if the geometrical distortion is static, and indeed many quantum chemical calculations have predicted large static dipole moments for small metal-atom clusters (see Ref. 28 for example). Experimentally these large dipoles are not seen, even at cryogenic temperatures where presumably thermal motions of the nuclei are less relevant.<sup>29</sup> This puzzle has attracted considerable recent attention and the current explanations involve nuclear motion (pseudo-rotation) whereby a small change in the distortion can produce a very different, sometimes opposite, dipole. Recent work within the Born-Oppenheimer approximation has suggested that the shapes of these clusters vary quite strongly over time<sup>1</sup> at room temperature with both pseudorotation and shape-inversion present, while at 20 K only the pseudorotation is present. At low temperatures these nuclear motions would be quantal, and when electronic degeneracies exist the motions may be anharmonic because of the conical intersection physics. Indeed a proper treatment will require a description of the coupled vibronic motions of the electrons and nuclei, and in this regime one may speak of the dynamic Jahn-Teller effect.<sup>2</sup> We tentatively suggest that the presence of a second such molecular cluster within the sub-asymptotic regime (see Eq. (35)) can significantly affect these vibronic phenomena, leading to a coupling of the vibrational as well

as the electronic motions of both molecules. If, during the course of these coupled motions at fixed intermolecular separation  $D$ , the instantaneous electronic gap  $\varepsilon_g$  satisfies the subasymptotic criterion (35) with significant probability, then one expects to see an anomalous  $D^{-3}$  vdW interaction similar to that discussed above for the sub-asymptotic regime of isosceles  $H_3$ .

## X. SUMMARY AND DISCUSSION

We first studied an idealized system consisting of two interacting equilateral  $H_3$  molecules separated by distance  $D$ , each molecule having frozen nuclear positions. We showed that this toy model exhibits “spooky” correlations between the fluctuating molecular electric dipole moments. These correlations do not decay with increasing intermolecular separation  $D$ , leading to a van der Waals interaction energy falling off as  $-D^{-3}$  (see Eq. (12)) rather than the conventional  $-D^{-6}$ . This interaction occurs in the ground state of the molecular dimer, and can be regarded as the zero-gap limit of the so-called “resonant interaction,” although the latter occurs only in an excited state when each molecule has a finite gap. This physics is only possible where each molecule has degenerate ground states coupled by the electric dipole operator. We suggested that a class of molecules worth exploring for the existence of such a spooky vdW interaction are those with an odd number of electrons, with discrete  $(2n + 1)$ -fold rotational symmetry about an axis in its ideal maximally symmetric configuration, and that therefore break inversion symmetry in that configuration. Equilateral  $H_3$  satisfies these criteria.

We also considered a small static Jahn-Teller distortion, leading to an isosceles  $H_3$  molecule. This system has a finite electronic gap and so two such molecules exhibit a conventional  $-D^{-6}$  dispersion interaction as  $D \rightarrow \infty$ . Using a limited CI model that can be solved analytically, we also found however that there can be an intermediate range of separations  $A < D < D_1$  (see Eqs. (35) and (36)) where the interaction energy is of form  $-A_3 D^{-3}$ , similarly to the undistorted equilateral case.

One of the most successful approaches for computation of dispersion interactions between “normal” gapped molecules is Symmetry-Adapted Perturbation Theory (SAPT, Ref. 30). It is clear that non-degenerate (single-determinant) perturbation theory, including SAPT, cannot work for the vdW interaction when there is a strictly degenerate ground state on each interacting molecule (as occurs for the toy equilateral  $H_3$  molecules studied in this paper). For systems with fairly small but finite gaps such as cases with static Jahn-Teller distortion, there certainly exists work within SAPT on the  $C_6$  vdW coefficient of the  $D^{-6}$  interaction, applicable at fully asymptotic separations, e.g., Ref. 31. The question arises, though, whether SAPT can obtain the  $D^{-3}$  interaction found in the present work above for slightly distorted (isosceles)  $H_3$  molecules in the sub-asymptotic regime of intermediate separations  $D$  (see Secs. VII A–VII C). This may be possible because the electronic ground state of isosceles  $H_3$  is no longer strictly degenerate but perhaps it requires a high order of perturbation theory in SAPT. We hope to investigate this in a future publication. One needs also to bear in mind that nuclear motions may

make such statically distorted calculations less relevant: see below.

H<sub>3</sub> is unfortunately unstable, but there exist odd-*N* clusters of metal atoms and other more rigid structures (e.g., Ref. 32) with equilateral (three-fold, 120°) or five-fold, or seven-fold... rotational symmetry, etc., and broken inversion symmetry. For two examples of such structures see Fig. 5. These may be more stable against geometric (Jahn-Teller) distortions than H<sub>3</sub> and so may exhibit dipole-allowed transitions between nearly degenerate ground states. Thus they may be candidates for a  $D^{-3}$  dispersion interaction, at least at sub-asymptotic separations (see the criterion of Eq. (35) for the sub-asymptotic regime). Furthermore, clusters of metal atoms are promising because they tend to have large hopping amplitude *t* between neighboring atoms, as evidenced by their ability to form highly conductive solids upon aggregation. These small cluster systems will tend to Jahn-Teller distort to produce large fixed dipoles but such dipoles are not seen in experiments on metal atom clusters. The likely explanation lies in small nuclear motions that induce large fluctuating dipoles (“pseudo-rotation”). We suggest that for dimers of these clusters, our novel vdW attraction would be mediated by coupled vibronic motions of both electrons and nuclei on both of the interacting molecules. If the molecules pass near the high-symmetry, electronically degenerate states sufficiently often during these combined motions, an appreciable weight of  $D^{-3}$  vdW interaction should be observable. The analysis in Ref. 24 and in the recent work of Requist, Tandetzky, and Gross<sup>33</sup> may be useful in analyzing this situation.

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