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

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Abstract

We consider the zero-temperature van der Waals interaction between two molecules, each of which has a zero or near-zero electronic gap between a groundstate 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 groundstate 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 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 groundstate 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 (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 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.

It is well known that a pair of molecules "a" and "b" in their dimer groundstate experience an atractive dispersion (van der Waals) 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

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

Here $|0\rangle_a$ annd E_{0a} are the many-electron groundstate and energy of molecule a. 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 constitutent nuclei. $|J_a\rangle$, E_{Ja} are many-electron eigenfunctions and eigenvalues of molecule a in isolation, and $|K_b>$, E_{Kb} are those of molecule b in islolation. $\hat{D} = \vec{D}/D$ 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 τ_{el} of the intramolecular dipolar fluctuations.

There is also clearly a problem with Eq (1) if both molecules have degenerate electronic groundstates so that there exist many-electron states $|J\rangle_a$ and $|K\rangle_b$ such that $E_{Ja} = E_{0a}$ and $E_{Kb} = E_{0b}$. 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. $C_6^{ab} \to \infty$). 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 [1],[2]) 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 microscopic theory gives $Z^{-5/2}$ [3]. 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 [4][5]. 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 acurate microscopic approaches yield $E(Z) \propto -Z^{-2}\left(\ln|z|\right)^{-3/2}$ [6],[4],[7][8] in the electromagnetlicaly non-retarded regime. These 2D and 1D nanosystems were argued [4],[9],[10],[11] to exhibit unconvential vdW powers because of their zero electronic energy gap and their low dimensionality (limiting the influence of coulomb screening). In a recent work [9], 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. One then wonders whether zero-dimensional systems (molecules) could exhibit similarly anomalous vdW interactions when their groundstates have a zero electronic energy gap: this provides an additional motivation for the present investigation, beyond the mathematical observation of a zero denominator in Eq (1).

I. 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 moleular pair as proposed above, the discussion following Eq (1) suggests that one needs to find a molecule with two strictly degenerate groundstates 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 groundstate, and previous work found that the theoretical H_3 conformation of minimum electronic groundstate energy would be a linear geometry, not a triangle. In general, even where a candidate degenerate molecule for these effects is stable, one can exepect 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 withn 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 the pure "type-C non-additivity "phenomenon in dispersion interactions between such molecules, as proposed in [9]). We first show that this non-interacting three-electron model for a single H_3 molecule has 2 exactly degenerate electronic groundstates for each allowed spin configuration. For each spin configuration we further show that the two groundstates are coupled by the dipole moment operator. We will then use a limited Configuration Interaction (CI) approach to a pair of H_3 molecules, leading to the spooky $-D^{-3}$ inter-interaction as described in general above. In the following section 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 a further Section we confirm these conclusions via a larger CI calculation using the package MOLPRO.

We label the three protons $i = 1, 2, 3$ (see Fg 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 form

$$H_{\uparrow}^{1\ electron} = \begin{pmatrix} \varepsilon & -t & -t \\ -t & \varepsilon & -t \\ -t & -t & \varepsilon \end{pmatrix} \tag{2}$$

where ε is the 1s energy and t is a "hopping" matrix element of the hamiltonian between

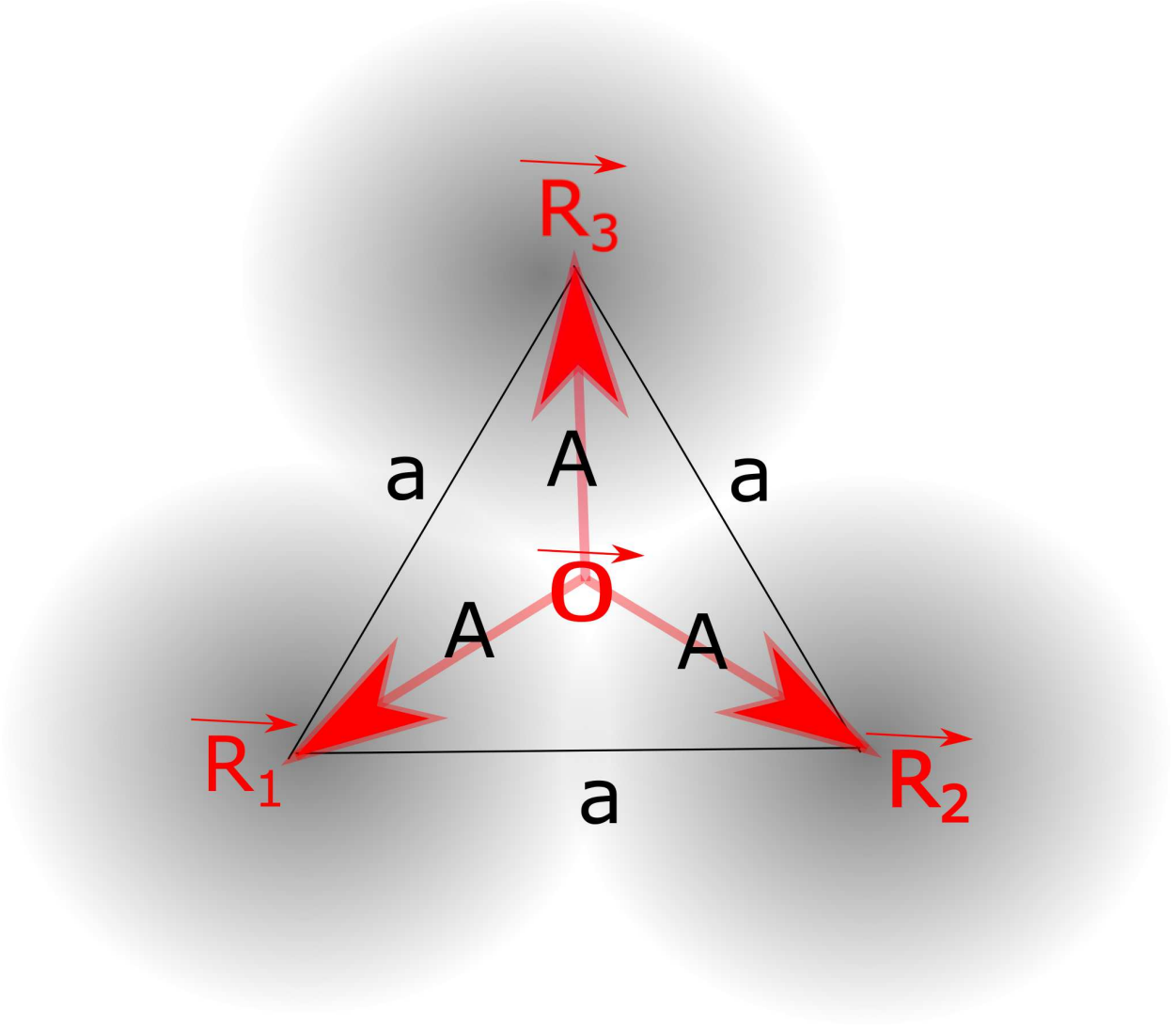

FIG. 1: Geometry of equilateral H_3

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

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

where $\vec{R}_i$ is the location of the i^{th} proton (see Fig 1 for molecular geometry and labelling). The neighbor overlap element α 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) are the three Bloch states

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

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 round the triangular molecule, respectively. The three Bloch states are eigenfunctions of the 120^0 rotation operator $\hat{\mathcal{R}}_{120}$, with eigenvalues $1, e^{i2\pi/3}$ and $e^{-i2\pi/3}$ respectively. The $+$ and $-$ states 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 (3) and (4)

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

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

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 groundstates $|G^+\rangle$ 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:

$$\left|G^+\right\rangle=\hat{c}^\dagger_{g\uparrow}\hat{c}^\dagger_{g\downarrow}\hat{c}^\dagger_{+\uparrow}\,|0\rangle\,, \quad \left|G^-\right\rangle=\hat{c}^\dagger_{g\uparrow}\hat{c}^\dagger_{g\downarrow}\hat{c}^\dagger_{-\uparrow}\,|0\rangle \tag{7}$$

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

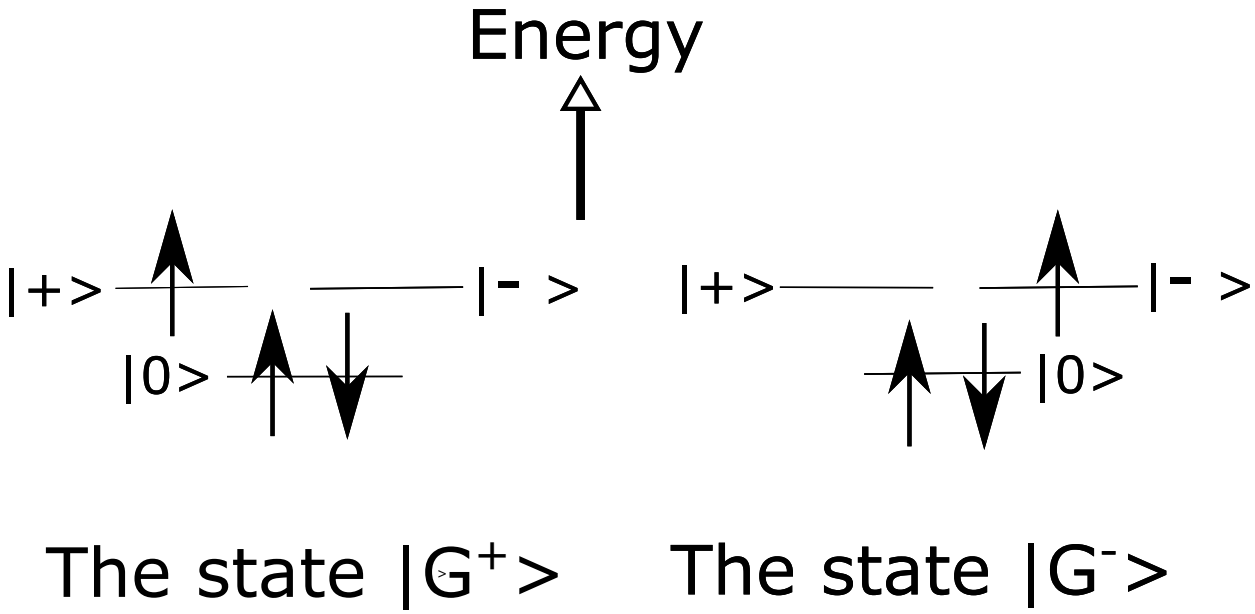

FIG. 2: Two degenerate independent-electron grounstates based on clockwise and anticlockwise Bloch britals

II. 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 1) simplifies to

$$\delta H_{ab} = e^2 D^{-3} \vec{X}_a . \vec{X}_b, \qquad \vec{X}_a = \sum_{i=1}^{3} \vec{r}_{ia} \tag{8}$$

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, keping only the two degenerate 3-electron groundstates on each molecule, leading to a fourfold product-basis set

$$\left|G^+\right\rangle_a \left|G^+\right\rangle_b, \quad \left|G^+\right\rangle_a \left|G^-\right\rangle_b, \quad \left|G^-\right\rangle_a \left|G^+\right\rangle_b, \quad \left|G^-\right\rangle_a \left|G^-\right\rangle_b \tag{9}$$

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

The intermolecular coupling matrix elements are

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

The vanishing of this matrix element can be understood because the two-molecule states $\left|G_a^+ G_b^+\right\rangle$ and $\left|G_a^- G_b^-\right\rangle$ 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 $\vec{X}_1.\vec{X}_2$ 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

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

We measure energies relative the groundstate energy of two independent H_3 molecules, and the CI hamiltonian then becomes extremely simple (with the states ordered as in Eq (9)):

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

Two independent bi-molecular states diagonalizing this Hamiltonian are

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

The state $|\Phi_e\rangle$ is the groundstate of the H_3−H_3 system, and its energy $-e^2A^2/\left(2D^3\right)$ 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.

III. 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 overt 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

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

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

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

pointing towards and away from nucleus # 3 of the H_3 triangle respectively. In the 3-electron groundstate 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 groundstates $|G^{up}\rangle$, $\left|G^{down}\right\rangle$ with the same dipole moments as in Eq (13):

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

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

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

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

$$|\Phi_e\rangle = i\left(|G^{up}\rangle_a\left|G^{down}\right\rangle_b - \left|G^{down}\right\rangle_a|G^{up}\rangle_b\right) \tag{17}$$

This exbibits $|\Phi_e\rangle$ 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 coefficents $\pm i$ 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 groundstate. 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 Hamiltian in the following basis of electric dipole states

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

giving

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

where $\mu = e^2A^2/2$. 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.

IV. 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 invariance under the 120-degree 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 $\left\langle G_a^+ G_b^+ \right| \vec{X}_a.\vec{X}_b \left| G_a^- G_b^- \right\rangle$ will therefore still be zero by the symmetry argument given above, and we expect $\left\langle G_a^+ G_b^- \right| \vec{X}_a.\vec{X}_b \left| G_a^- G_b^+ \right\rangle$ will still be non-zero. The question is whether these two degenerate states are still groundstates. We have set up a 9×9 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 groundstates for all positive t except for $t = 0$ exactly. For $t = 0$ the three exactly degenerate groundstates have no double occupation of any proton site. We also verified explicitly that

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

However, as t decreases towards zero, the gap from the groundstate 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.

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

We also used 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 [9]), 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 groundstate at all the D values considered. Two 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 [9]) are assisting rather than hindering the type-C (inter-atom hopping) polarizability, in the present geometry.

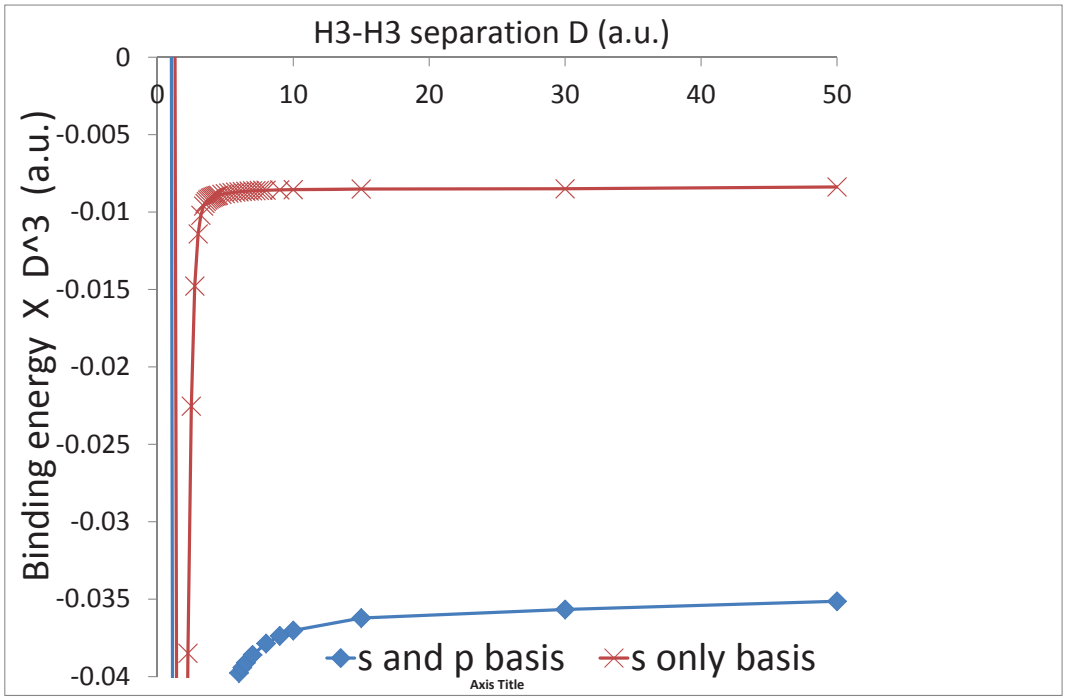

FIG. 3: Demonstration that the interaction energy of two H3 molecules falls off as $E \approx -C_3 D^{-3}$, both with an s-only basis and with an s+p basis. Electron-electron interactions are retained within and between molecules in both cases

V. 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 [12], causing broken rotational symmetry of the proton configuration in the groundstate. 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 groundstate, 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 ε_g Candidate systems for this situation might include transition or rare earth metal clusters where the observed enhanced rigidity of the bulk metal (comapred 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 exloration 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 ε_g is small enough.

VI. 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 $\vec{R}_1 = -b\hat{x}/2 - h\hat{y}/3$, $R_2 = +b\hat{x}/2 - h\hat{y}/3$, $\vec{R}_3 = \frac{2}{3}h\hat{y}$. (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

$$\hat{H} = \varepsilon + \begin{pmatrix} 0 & -t & -t' \\ -t & 0 & -t' \\ -t' & -t' & -\Delta \end{pmatrix} \tag{19}$$

where t' is the hopping element to/from the apex, atom #3 (see fig. 4) and Δ is the additional energy of an electron on proton 3 as a result of orbtal compression in the groundstate. Here for an acute isosceles triangle we expect $\Delta < 0$ and $0 < t' < t$ so that $\delta \equiv t' - t < 0$

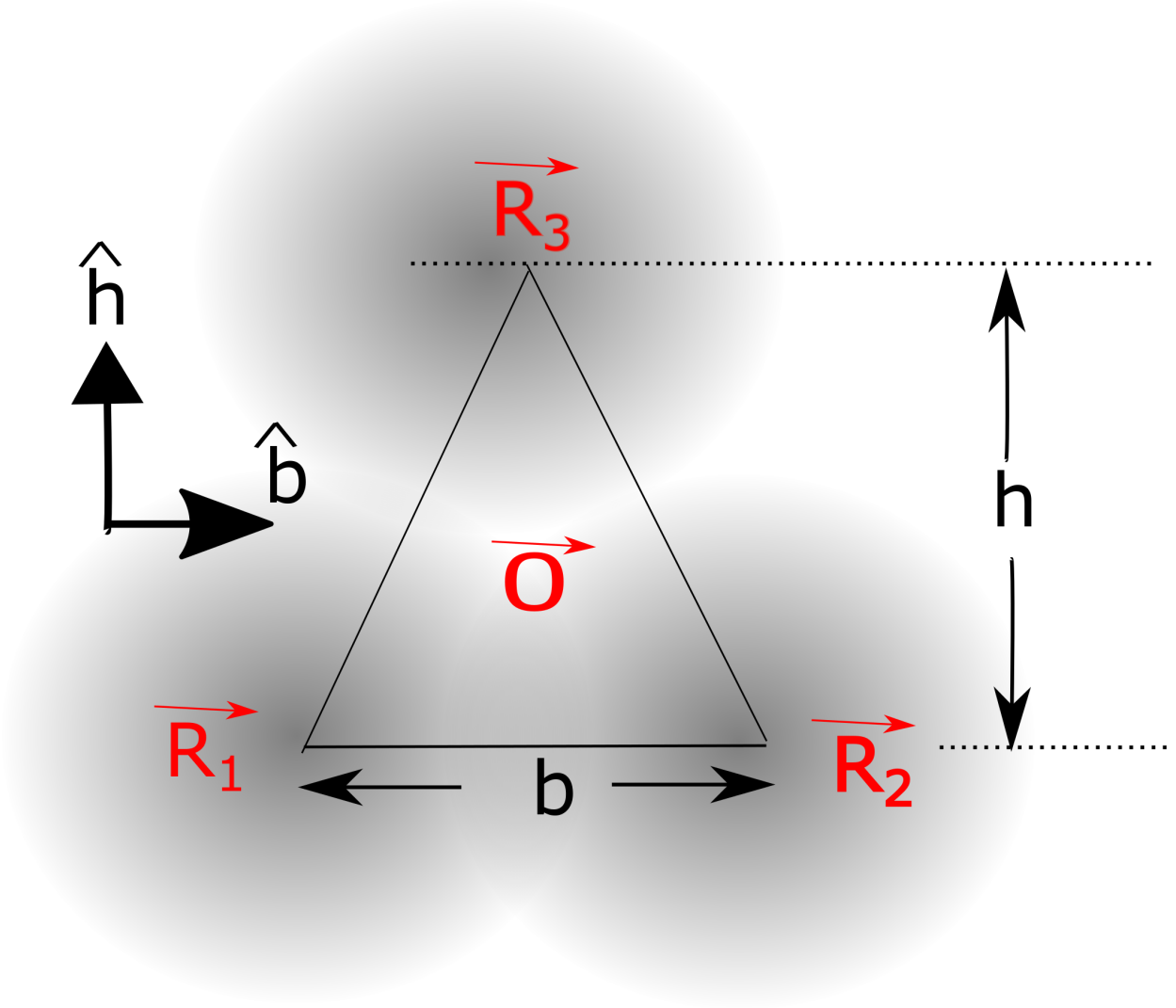

FIG. 4: Geometry of isosceles H_3

For an obtuse isosceles triangle, $\Delta > 0$ and $\delta > 0$. The eigenvalues of (19) are

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

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

$$\varepsilon^{(3)} = \varepsilon + t \tag{21}$$

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 $\theta_3 < 90^0$, $\left|\vec{R}_3 - \vec{R}_1\right| > \left|\vec{R}_2 - \vec{R}_1\right|$) state (1) is the one-electron ground orbital and $\varepsilon^{(3)} > \varepsilon^{(2)} > \varepsilon^{(1)}$. If the isoscles triangle is only slightly distorted from an equilateral triangle then Δ and $\delta \equiv t' - t$ are both small. In this region we can Taylor-expand (21)

giving an energy gap

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

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 ocupied, and for the acute triangle case the groundstate has the $\varepsilon^{(2)}$ orbital singly occupied. Equally, for an obtuse isosceles H_3 molecule the groundstate 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,

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

where the normalizing factors N_i depend on the direct overlaps $\alpha_{23} = \alpha_{13}$, α_{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

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

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

$$\begin{aligned}
\eta_1 &= \frac{-|e|\,N_1}{3}\left(-\frac{1}{2}\left(\frac{\varepsilon^{(2)}+\Delta-\varepsilon}{t'}\right)^2(1+\alpha)+2-\frac{1}{2}\frac{\varepsilon^{(2)}+\Delta-\varepsilon}{t'}\alpha_{23}\right)h \\
\eta_2 &= \frac{-|e|\,N_2}{3}\left(-\frac{1}{2}\left(\frac{\varepsilon^{(1)}+\Delta-\varepsilon}{t'}\right)^2(1+\alpha)+2-\frac{1}{2}\frac{\varepsilon^{(2)}+\Delta-\varepsilon}{t'}\alpha_{23}\right)h \\
\eta_3 &= \frac{-|e|\,2N_3\,(1-\alpha)}{3}h \\
\eta_{23} &= -|e|\sqrt{N_2N_3}\left(-\frac{1}{2}\frac{\varepsilon^{(1)}+\Delta-\varepsilon}{t'}+\frac{1}{2}\alpha_{23}\right)b
\end{aligned}$$

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

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

$$|B\rangle = c^\dagger_{1\uparrow} c^\dagger_{1_\downarrow} c^\dagger_{2\uparrow} |0\rangle\,, \quad |S\rangle = c^\dagger_{1\uparrow} c^\dagger_{1_\downarrow} c^\dagger_{3\uparrow} |0\rangle$$

These states are separated by a small gap ε_{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 groundstate, while the state $|S\rangle$ with a dipole pointing to the apex or summit ("S") is the groundstate for the obtuse case. The dipole matrix elements for a single molecule are

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

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 ε_g we need only keep, as our two-molecule product basis, the groundstate and lowest 3 excited noninteracting states of the $H_3{-}H_3$ complex, namely $|S\rangle_a\,|S\rangle_b\,,\ |S\rangle_a\,|B\rangle_b\,,\quad |B\rangle_a\,|S\rangle_b\,,\quad |B\rangle_a\,|B\rangle_b$ in that order. In this basis the bi-molecular hamiltonian matrix (relative to two isolated groundstate molecules), including the dipole interaction $\delta H = e^2 X_a.X_b/D^3$ between the molecules, is

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

where

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

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

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

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_3 molecule, though the coefficients $a, \beta, c, ..., g$ 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_3.molecule, invalidating the present analysis.

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

The eigen-energies of the interacting isosceles H_3-H_3 system (measured from the ground-state of two isolated H_3 units), from diagonalization of (26), are as follows:

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

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

$$E_{II} = \varepsilon_g + \frac{\beta + f}{D^3} \tag{30}$$

$$E_I \ = \varepsilon_g + \frac{\beta - f}{D^3} \tag{31}$$

B. Asymptotic regime of isosceles H_3- H_3 interaction: conventional fixed dipolar, vdW and (excited) resonant interactions

Since the (frozen) isosceles distortion away from an equilateral configuration has introduced an energy gap ε_g and a large permanent electric dipole $\vec{d}_B$ in the H_3 groundstate, one might initially expect that the groundstate H_3-H_3 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

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

where $\left| \vec{d}_{\max} \right|$ 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 lowest to highest:

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

This state III is the groundstate of the H_3-H_3 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_3 molecules have the same alignment so that $a > 0$). The next-lowest energies are

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

Since $\beta < 0$ and $f > 0$ (see (27)), state I with energy E_I is the first excited state of the H_3 dimer. Its energy is just below ε_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 [13]. Such resonant excited states depend on the two gaps having the same nonzero value ε_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[14]. 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 moleular dimer state from (26), labelled IV, has an energy close to twice the gap energy,

$$E_{IV} = 2\varepsilon_g + O\left(D^{-3}\right) \tag{34}$$

C. Subasymptotic regime of spooky D^{-3} vdW interaction between isosceles H_3 molecules

We will now show that if the gap ε_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 relevent regime is

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

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:

$$E_I \approx \varepsilon_g + \frac{\beta - f}{D^3} \;\; bimolecular\ groundstate,\ spooky\ attractive\ vdW \tag{36}$$

$$E_{II} \approx \varepsilon_g + \frac{\beta + f}{D^3} \;\; excited\ bimolecular\ state \tag{37}$$

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

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

In this regime the terms proportional to ε_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 groundstate, and not an excited state as in the ususal 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 $\left(1\text{Å}\right)(|e|)$ the outer limit of the subasymptotic spatial regime from (35) is at $D_1 \approx 2.5$ Å which lies in the overlap region of electronic clouds where the present approach is not valid. However with a gap of ε_g =0.01 eV and the same dipole moment we find $D_1 \approx 12$ Å.which leaves a viable sub-asymptotic region. Larger dipole moments and smaller gaps will extend D_1 to larger values.

VII. OTHER MOLECULES LIKELY TO HAVE ELECTRONIC DEGENERACY SIMILAR TO 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 groundstate, were that an individual molecule has two degerate electronic groundstates that are coupled by the dipole operator. To achieve this in a similar manner to the equilateral 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 $\hat{R}_{360^0/N}$.

(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, $N = 2n+1, \quad = 1, 2, 3, ...$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 $\Psi_1\left(\vec{\xi}\right) \equiv \left\langle \vec{\xi} \right| |+\rangle$, $\Psi_2\left(\vec{\xi}\right) = \left\langle \vec{\xi} \right| |-\rangle = \Psi_1^*\left(\vec{\xi}\right)$ that are both eigenstates of the rotation operator $\hat{\mathcal{R}}_{360/(2n)} = \hat{\mathcal{R}}_{180/n}$. Here for an M-electron molecule we have denoted

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

Since for even-order rotational symmetry Ψ_1 and Ψ_2 are eigenstates of $\hat{\mathcal{R}}_{180/n}$, they are also eigenstates of $\left(\hat{\mathcal{R}}_{180/n}\right)^n = \hat{\mathcal{R}}_{180}$:

$$\hat{\mathcal{R}}_{180}\Psi_1 = \theta_1\Psi_1, \qquad \hat{\mathcal{R}}_{180}\Psi_2 = \theta_1^*\Psi_2 \tag{40}$$

Further since two 180^0 rotations produce no net effect we have $\left(\hat{\mathcal{R}}_{180}\right)^2 = \hat{I}$ and so in (40) we have $\theta_1^2 = 1 \Longrightarrow \theta_1 = 1$ or -1

However the 180^0 rotation operator $\hat{\mathcal{R}}_{180}$ is in fact the spatial coordinate inversion operator in the plane perpendicular to the rotational symmetry axis:

$$\hat{\mathcal{R}}_{180}\Psi\left(\vec{\xi}\right) \equiv \Psi\left(\vec{\xi}'\right)$$

where for an M-electron molecule

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

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

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

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 $\langle -|\, \vec{d}_\perp \,|+\rangle$

$$\langle -|\, \vec{d}_\perp \,|+\rangle \equiv d_x \hat{x} + d_y \hat{y} = -|e| \int \left(\Psi_1 \left(\vec{\xi}\right)\right)^2 (\vec{r}_{1\perp} + \vec{r}_{2\perp} + ... + \vec{r}_{M\perp})\, d^{3M}\xi \qquad (41)$$

But $\left(\Psi_1 \left(\vec{\xi}\right)\right)^2 = \left(\theta_1^{-1} \Psi_1 \left(\vec{\xi}'\right)\right)^2 = \theta_1^{-2} \left(\Psi_1 \left(\vec{\xi}'\right)\right)^2 = 1 \left(\Psi_1 \left(\vec{\xi}'\right)\right)^2$. Thus Ψ_1^2 is even under the inversion $\vec{\xi} \to \vec{\xi}'$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 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,...)

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 H_3 problem treated above.

Thus to obtain a D^{-3} vdW interaction in a similar fashion to that obtained for a pair of H_3 molecules above, we need to search for molecules that have discrete odd rotational symmetry. Regular (2n+1)-gons satisfy this when $n = 1, 2, 3, ...$ 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.

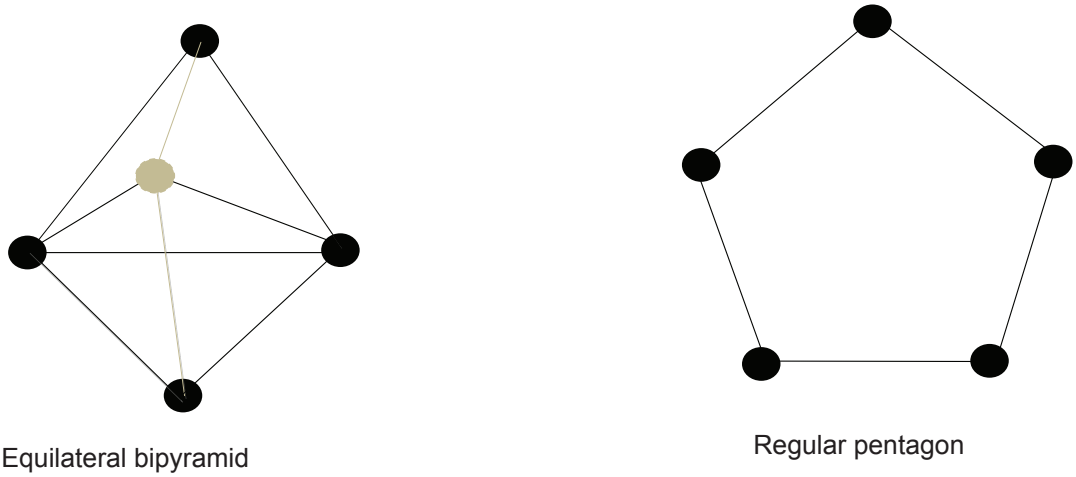

FIG. 5: Two geometries conducive to spooky vdW forces

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 groundstates states to be well separated from the first exicted 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 discrete (90^0) rotational symmetry and therefore has 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.

VIII. 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 [15] for example). Experimentally these large dipoles are not seen, even at cryogenic temperatures where presumably thermal motions of the nuclei are less relevant.[16]. 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 [1] at room temperature with both pseudorotation and shape-inversion present, while at 20K 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 dymamic Jahn-teller effect ([2]). We tentatively suggest that the presence of a second such molecular cluster within the sub-asymptotic regime (see (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 ε_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.

IX. 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"corelations 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 groundstate 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 groundstates 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.

H_3 is unfortunately unstable, but there exist odd-N clusters of metal atoms and other more rigid structures (e.g. [17]) with equilateral (three-fold, 120^0) 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 $\bar{H}_3$, and so may exhibit dipole-allowed transistions between nearly- degenerate groundstates. 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). Furthernore, 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 ("pdeudo-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 sufficienly often during these combined motions, an appreciable weight of D^{-3} vdW interaction should be observable.

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