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Signature of van der Waals Interactions in the Cumulant Density Matrix

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Here we propose and implement a universal signature of the van der Waals interactions based on the cumulant part of the two-electron reduced density matrix (2-RDM). Due to the connected property of the cumulant, we can use it to detect the van der Waals interactions between two molecular moieties. In particular, we use the squared Frobenius norm of the cumulant of the 2-RDM, which has been previously shown to provide a size-extensive measure of the electron correlation. As two moieties are separated to infinity, the cumulant Frobenius norm exhibits an r^{-6} decay to its asymptotic limit, providing a density-based measure of the van der Waals interaction. We study this signature of van der Waals forces in a collection of small molecules of varying geometries. These computations agree with experimental trends of known literature values.

I. INTRODUCTION

Van der Waals forces are universally experienced by any two molecules. This ubiquity makes them of utmost importance, as seen in their prevalence from microscopic systems involving protein interactions to macroscopic bodies exhibiting adhesion.[1–4] However, computing van der Waals forces and measuring their signature is particularly challenging.[5] This is due to the short-range impact of the forces, the fast decay rate of the energy, which is r^{-6} where r is the internuclear separation, and most importantly, their origin in intermolecular electron correlation.[6]

Here we propose a density-based approach to measuring and studying van der Waals interactions by using of the cumulant of the two-electron reduced density matrix (2-RDM).[7,8] Recent work by Via-Nadal, Rodríguez-Mayorga, and Matito[6] has shown that van der Waals forces can be detected in the intracule of the pair density. We extend this approach by using the cumulant part of the 2-RDM which includes the connected part of the pair density as well as additional information. Because van der Waals forces arise from the interaction of induced dipoles, the forces arise from intermolecular electron correlation. The participating electrons on each moiety are statistically dependent on each other, and consequently, the van der Waals forces are contained in the part of the 2-RDM in which the two electrons are statistically dependent, known as the cumulant (or connected) part of the 2-RDM.[7–10] The van der Waals forces are not describable with a mean-field method or a traditional density functional method.[11]

To obtain a signature of the van der Waals interaction, we consider the squared Frobenius norm of the cumulant, the trace of the squared cumulant.[12–14] The squared Frobenius norm of the cumulant, which is nonnegative and size extensive, meaning that it scales linearly with system size, has been used as a measure of electron correlation and electron entanglement between different chemical domains. Here, we use the squared Frobenius norm to detect the electron entanglement between the two molecular moieties experiencing the van der Waals interaction. Because the squared Frobenius norm is size extensive, we can use its deviation from its value at infinite separation to measure the electron correlation associated with the interaction. We show that in the presence of van der Waals interactions the square Frobenius norm exhibits an r^{-6} decay with the distance r between two molecules. This density-based analysis provides a fundamental, correlation-driven perspective on the nature of the van der Waals forces. Applications of the cumulant norm are made to a selection of small atoms and molecules to demonstrate the utility of the norm as a detector and quantifier of van der Waals interactions.

II. THEORY

A. Cumulant of the 2-RDM

To treat van der Waals forces, we begin with a general construction of the 2-RDM and its cumulant part. Integrating the N-electron density matrix over all electrons save two yields the 2-RDM

$$^{2}D(1,2;\bar{1},\bar{2}) = \int D(123..N;\bar{1}\bar{2}3..N)d3..dN, \qquad (1)$$

which describes the probability distribution of two electrons in the field of the remaining N electrons.[15–18] One- and two-electron properties of the electronic system are captured by the 2-RDM because electrons are indistinguishable with pairwise interactions.[18] The 2-RDM can be described mathematically as the sum of the wedge product between one-electron reduced density matrices (1-RDMs), ^{1}D, and a cumulant term, $^{2}\Delta^{jk}_{kl}$,[8,9,12,13,15,16,19–24]

$$^{2}D^{jk}_{kl} = 2\,^{1}D^{i}_{k} \wedge {}^{1}D^{j}_{l} + {}^{2}\Delta^{jk}_{kl}, \qquad (2)$$

where the 2-RDM is normalized to $N(N-1)$ and the Grassmann wedge product[7,25,26] is an antisymmetric ten-

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$$2\,{}^1D^i_k \wedge {}^1D^j_l = {}^1D^i_k\,{}^1D^j_l - {}^1D^i_l\,{}^1D^j_k. \qquad (3)$$

This cumulant (or connected) term is the part of the 2-RDM that cannot be written as a wedge product of lower RDMs.[7,27] Because the cumulant term is the part of the 2-RDM in which the two electrons are statistically dependent, it scales linearly with the size of the molecular system (size extensive). The cumulant 2-RDM's size extensivity formally follows from its derivation from an exponential generating functional.[7] Reconstruction of the 3- and 4-RDMs in terms of the cumulant 2-RDM has been used in electronic structure methods like the contracted Schrodinger equation method,[28,29] the anti-Hermitian contracted Schrodinger equation method,[30–32] canonical transformation,[33] the parametric 2-RDM method,[34,35] driven-similarity renormalization group,[36] and density cumulant functional theory.[37,38]

The squared Frobenius norm of the cumulant 2-RDM

$$||{}^2\Delta||^2_F = \mathrm{Tr}[({}^2\Delta)^2], \qquad (4)$$

is a nonnegative, size-extensive quantity that is a useful measure of electron correlation and entanglement.[12,13] In a pure-state quantum system the squared Frobenius norm of the cumulant is nonzero if and only if the system is not correlated. Because the cumulant norm is sensitive to the correlation of electrons (orbitals) on two separated molecules, it can serve as a measure of the electron entanglement of the molecules. When the two molecules are infinitely separated and not spin entangled, the squared Frobenius norm will equal the sum of each molecules's squared Frobenius norm. The change in the Frobenius norm as the separation between the molecules decreases reflects the intermolecular entanglement of the electrons, which is the quantum-mechanical origin of the intermolecular force or potential.

B. Measures of van der Waals interactions

The cumulant's squared Frobenius norm can be applied to detect and quantify intermolecular forces. While the change in the energy with distance gauges the intermolecular potential's contribution to the potential energy surface, the cumulant norm reflects the entanglement of the electrons across the molecules that generates the intermolecular potential. Recent work by Via-Nadal, Rodríguez-Mayorga, and Matito[6] has established that the signature of the van der Waals interactions can be calculated for H and He based on the intracule pair density, which decays at a rate of r^{-3}. Here we employ the cumulant 2-RDM and its squared Frobenius norm rather than the correlated part of the intracule pair density to study these interactions. A potential computational advantage of the cumulant 2-RDM is that can be used to detect the van der Waals forces in any representation—position, momentum, or otherwise. While the cumulant 2-RDM's norm is invariant to one-electron unitary transformations,[39] its diagonal part, such as the correlated pair density in the position representation, is not invariant.

The distance dependence of the cumulant 2-RDM for van der Waals forces can be estimated from: (1) the scaling of the van der Waals energy with respect to distance and (2) the scaling of the effective van der Waals Hamiltonian with respect to distance. It is well-known that the energy of the van der Waals potential scales as r^{-6} and that the effective van der Waals Hamiltonian scales as r^{-3}.[40] The electronic energy is expressible in 2-RDM theory as

$$E = \mathrm{Tr}({}^2K\,{}^2D), \qquad (5)$$

where ${}^2K$ is the two-electron reduced Hamiltonian containing the one-electron and two-electron molecular integrals. If we replace the ${}^2K$ by an effective two-electron reduced Hamiltonian for the van der Waals interactions ${}^2K_{\mathrm{vdW}}$ and the ${}^2D$ by its cumulant part ${}^2\Delta$, we obtain a theoretical expression for the van der Waals energy

$$E_{\mathrm{vdW}} \approx \mathrm{Tr}({}^2K_{\mathrm{vdW}}\,{}^2\Delta). \qquad (6)$$

Because the van der Waals energy and reduced Hamiltonian are known to scale as r^{-6} and r^{-3} respectively, we have that the cumulant 2-RDM scales as r^{-3}. This result is consistent with that obtained for the correlated pair density derived by Matito and co-workers.[6] From the definition of the squared Frobenius norm, we have that in the case of van der Waals interactions the squared Frobenius norm of the cumulant 2-RDM scales as r^{-6}.

III. APPLICATIONS

We apply this theory to model van der Waals forces in a variety of small atomic and molecular dimers and compare these results to experimental data. The variety of geometries in these test systems indicates the relevance for this method for more complex systems.

A. Computational Methodology

All of the 2-RDM calculations were performed using PySCF.[41] In particular, the 2-RDMs were computed with the coupled cluster singles-doubles (CCSD)[42] method in a correlation-consistent double-zeta basis set (cc-pVDZ).[43–46] The 2-RDMs in the molecular-orbital basis set were obtained for dimer separation distances between 4 and 20 Å at 0.5 Å intervals. With these density matrices we computed the cumulant part of the 2-RDM and the associated squared Frobenius norm. We then fit this data to r^{-6}, as this is the asymptotic scaling of the van der Waals force. Tables S1 through S3 of the Supplemental Information report the computed cumulant norms employed in the fits, and Tables S4 through

S13 of the Supplemental Information report the geometries of all studied molecular dimers at a separation of 6 Å.

B. Results

First, we consider the classic, isotropic van der Waals interactions in the argon noble gas dimer. As shown in Fig. 1a, the squared Frobenius norm of the cumulant increases and then plateaus as the argon atoms are separated in the range of 4 Å to 12 Å. The Frobenius norm plateaus at a finite, non-zero value that reflects the electron correlation within each of the argon atoms. The decrease in the norm as the atoms are brought together is due to the electron correlation between the argon atoms which gives rise to the van der Waals forces. The circles in the plot represent computed Frobenius norms while the solid line denotes an $\alpha/r^{-6}+\beta$ least-squares fit. As expected from the theory, we find that the r^{-6} fit is highly accurate. For comparison, we show the errors from r^{-5}, r^{-6}, and r^{-7} least-squares fits in Fig. 1b. Results confirm that the data has an r^{-6} asymptotic decay.

There is also high agreement between the data of the cumulant 2-RDM's squared Frobenius norm and the r^{-6} decay for the anisotropic interaction of the carbon dioxide dimer, as seen in Fig. 2a. This dimer was in a parallel geometry, pulled apart from the carbon centers. Inspection of Fig. 2b indicates the preference of the r^{-6} fit, relative to similar fits for r^{-5} and r^{-7}, in capturing the system behavior for a larger variety of distances. This indicates the potential scope of this method, as it captures the electronic interactions of molecular dimers of differing geometries and sizes. The success of the method for molecules with a variety of orientations suggests its potential utility for larger, biological systems.

TABLE I: The R^2 value for fitting the square of the cumulant 2-RDM's Frobenius norm of each of the following molecules to the decay functions r^{-5}, r^{-6}, and r^{-7} are shown, indicating that the computed data is consistent with the predicted r^{-6} decay.

	R^2		
Molecule	r^{-5}	r^{-6}	r^{-7}
F_2-F_2	.989	.999	.987
Ar-SO_2	.986	.999	.997
BH_3-BH_3	.987	.999	.996
Ar-CO_2	.988	.999	.987
Ar-Ar	.995	.999	.990
CH_4-CH_4	.983	.997	.994
NH_3-NH_3	.991	.996	.988
Be-Be	.991	.999	.963
CO_2-CO_2	.997	.998	.997
SO_2-SO_2	.983	.997	.994

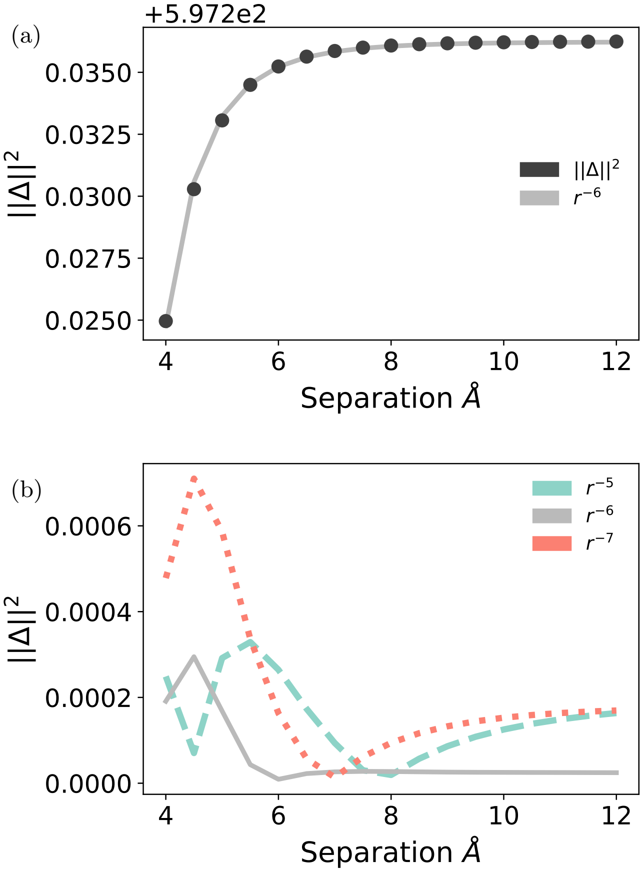

FIG. 1: In the argon dimer (a) the squared Frobenius of the cumulant 2-RDM as a function of Ar-Ar distance shows the decay of the van der Waals interaction with distance. The black circles indicate the squared Frobenius norm of the cumulant 2-RDM while the solid gray line indicates an r^{-6} function fitted to the squared Frobenius norm. The errors of r^{-5} (teal dashed line), r^{-6} (solid gray line), and r^{-7} (coral dotted line) functions fitted to the squared Frobenius norm of the cumulant 2-RDM reveal in (b) that the data is best approximated by the r^{-6} decay. The +5.972e2 denotes a shift of vertical axis's scale.

In order to make this relationship explicit, the R^2 values for these fits are tabulated in Table I. As is evident from this table, the dimer systems universally achieved highest accuracy fitting results with decays of $C_6 r^{-6}$, where C_6 is a density-based van der Waals coefficient. This indicates the validity of the squared Frobenius norm of the cumulant 2-RDM as a measure of the van der Waals signature, which decays at a rate of r^{-6}. This relationship holds for small molecules with a variety of geometries, suggesting the versatility of the approach.

Moreover, it is possible to compare loosely the density-based C_6 values from the fitting with the energy-based literature values. This comparison is tabulated in Table II. We do see discrepancies in the resulting data when

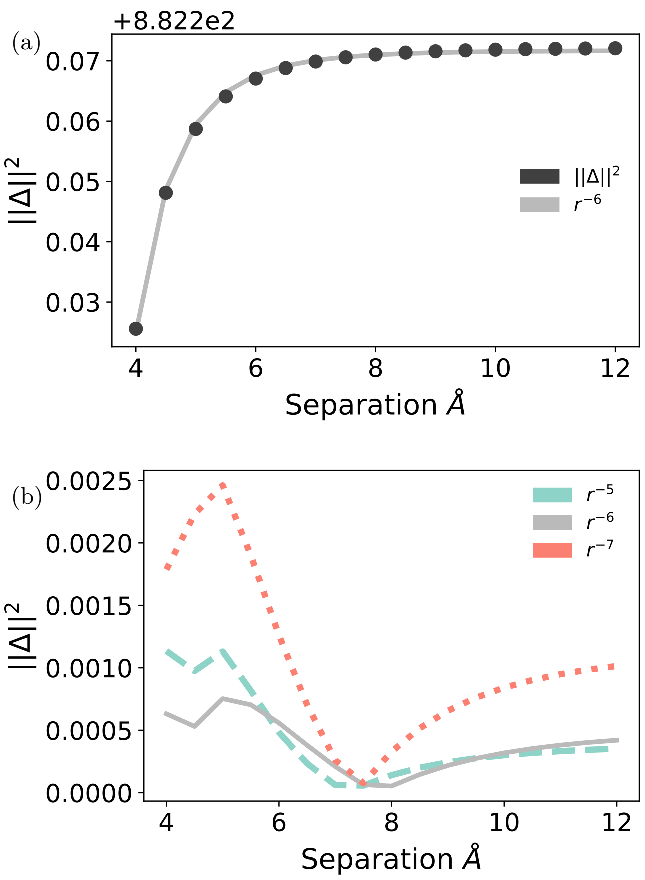

FIG. 2: In the carbon dioxide dimer (a) the squared Frobenius of the cumulant 2-RDM as a function of the intermolecular distance shows the decay of the van der Waals interaction with distance. The black circles indicate the squared Frobenius norm of the cumulant 2-RDM while the solid gray line indicates an r^{-6} function fitted to the squared Frobenius norm. The errors of r^{-5} (teal dashed line), r^{-6} (solid gray line), and r^{-7} (coral dotted line) functions fitted to the squared Frobenius norm of the cumulant 2-RDM reveal in (b) that the data is best approximated by the r^{-6} decay. The $+8.822e2$ denotes a shift of vertical axis's scale.

comparing the energy- and density-based results due to significant differences in the two quantities. The van der Waals forces can in principle affect the cumulant 2-RDM norm more or less than the energy. The energy is weighting the change in the cumulant 2-RDM through its trace with the two-electron reduced Hamiltonian matrix.

Visually, we can see the coherence between the trends in the two methods in the linear regression shown in Fig. 3. This model has an R^2 value of 0.84, indicating consistency between the trends in the literature and the trends in our data. This agreement suggests validity in the data, as it is impossible to compare the values explicitly due to the difference between the decay of the intermolecular energies and the decay of the intermolecular part of the cumulant density matrix.

TABLE II: Comparison of the calculated density-based C_6 values with the energy-based C_6 literature values

Molecule	Computed $\lvert C_6\rvert$	Literature $\lvert C_6\rvert$[a]
F_2-F_2	9.39	-
Ar-SO_2	23.2	-
BH_3-BH_3	43.6	-
Ar-CO_2	17.7	114.5
Ar-Ar	47.0	64.4
CH_4-CH_4	63.3	130
NH_3-NH_3	84.9	89.0
Be-Be	188	214
CO_2-CO_2	193	159
SO_2-SO_2	557	294

[a] References for Ar-CO_2[47], Ar[48], CH_4[49], NH_3[50], Be[51], CO_2[52], SO_2[53], as tabulated by Vydrov and Van Voorhis[54]

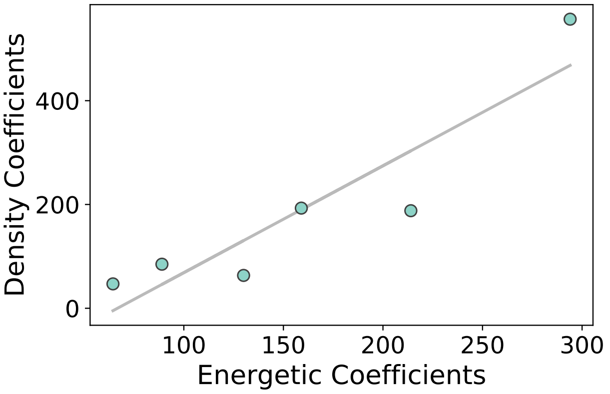

FIG. 3: Linear regression of the calculated density C6 coefficients versus the literature energetic C6 coefficients is shown.

IV. DISCUSSION AND CONCLUSIONS

In this paper we propose and implement a universal signature of the van der Waals interactions based on the cumulant part of the two-electron reduced density matrix (2-RDM). The cumulant is the connected part of the 2-RDM[7,8] which is not only size extensive and but also invariant to unitary transformations of the orbitals.[39] This invariance extends recent work by Via-Nadal, Rodríguez-Mayorga, and Matito[6] who examined the use of the pair density to detect van der Waals interactions. Previously, Juhász and Mazziotti[12,13] showed that the squared Frobenius norm of the cumulant provides a size extensive measure of electron correlation and entanglement. Here we apply this cumulant norm to quantify the electron entanglement between molecules that gives rise to the van de Waals attraction. Like the energy, we show that the cumulant norm has an r^{-6} decay with respect to molecular separation. The cumulant-based signature of van der Waals forces provides a direct measure of the entanglement of electrons on the separated molecules that is responsible for the van der Waals potential.

Computations with a selection of small molecules confirm the r^{-6} decay of the squared Frobenius norm of the cumulant with respect to molecular separation. These results also imply that the cumulant 2-RDM has a r^{-3} decay which is consistent with the theoretical result presented earlier in the paper. The density-based signature for van der Waals forces provides a systematic approach to quantifying these forces as well as connecting them to the underlying electron entanglement between the molecules. Many electronic structure methods such as conventional density functional theory have difficulty capturing the r^{-6} decay of van der Waals forces with molecular separation.[5,55] These difficulties arise from an incorrect description of the electron correlation. The description of van der Waals forces in terms of the cumulant 2-RDM provides greater understanding of the inner workings of these forces but also a mechanism for assessing their description by various electronic structure methods.

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