An Efficient Coupled Dipole Method for the Accurate Calculation of van der Waals Interactions at the Nanoscale

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Abstract The van der Waals (VDW) force arises from purely quantum mechanical charge fluctuations and is variously called a dispersion or London or Casimir force. This often considered as weak, yet ubiquitous, attractive interaction is important in many nanoscale systems. This chapter provides an overview of the Coupled Dipole Method (CDM), an atomistic and accurate computational method widely adopted to predict the VDW forces between dielectric nanomaterials. There is a concern about the burden of memory and computing time needed to solve eigenvalue problems by either diagonalization or iteration, which have hindered the implementation of CDM for large systems. Here, an efficient way, named trace-CDM (TCDM), is presented. TCDM uses the simple fact that the trace of a square matrix is equal to the sum of its eigenvalues and thus calculates the accurate VDW energies without solving for the eigenvalues. Four examples are solved to demonstrate the advantages of the method.

Keywords van der Waals (VDW) forces and interactions · Dispersion force · London force · Casimir force · Coupled dipole method (CDM) · Trace-CDM (TCDM) · Nanoscale · Dielectric nanomaterials · Diagonalization · Iteration · VDW energies

1 Introduction

The van der Waals (VDW) interaction between atoms and molecules composing or being near a soft or hard condensed matter has always been one of the major research interests in diverse science and engineering fields. At separations large compared to atomic dimensions such that the overlap of electronic densities is negligible, atoms, molecules, self-assemblies, and surfaces interact via VDW dispersion forces giving arise to physical adsorption, atomistic friction, surface tension, and the aggregation

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and stability of nanomaterials. This interaction is often considered as a weak, and thus less significant, force in macroscopic systems. However, the degree of importance of VDW force varies for different systems and thus cannot be universally summarized. After all, the very existence of the attraction between any two neutral non-polar atoms or molecules was the mystery that made many scientists puzzle for a long time even after Johannes Diderik van der Waals empirically modified the ideal gas law and introduced the well-known van der Waals equation of state [1–5]

$$\left(P+\frac{a}{V^2}\right)(V-b)=Nk_BT \tag{1}$$

Here k_B, V, P, T, and N are the Boltzmann constant, total volume, pressure, temperature, and the number of gas atoms, respectively. The constants a and b in the correction terms can be empirically determined. The correction term in volume (b) represents the reduced accessible volume for each atom due to the repulsion from other atoms that already have occupied the volume b. The correction term in pressure (a/V^2) implies that the atoms at the boundary have less kinetic energy than those in the interior due to the attractive force exerted by other atoms. The attractive correction term in potential energy of atoms is proportional to $1/V^2$, i.e., proportional to $1/r^6$ if r is the mean separation of the gas atoms. The identity of this mysterious attractive force observed between neutral atoms was unsolved until the introduction of quantum mechanics. In 1930, London [6–10] solved the many-electron Schrödinger equation by second-order perturbation theory and represented the energy gain by the attractive force with an integral over the dynamic polarizaiblites of each atom. London's derivation of the VDW dispersion interaction is thus considered as one of the major early successes of quantum mechanics [3].

In short, the problem of calculating the interaction energy between two atoms reduces to a solution of the Schrödinger equation with a Hamiltonian:

$$\mathrm{H}=\mathrm{H}_1+\mathrm{H}_2+\mathrm{V} \tag{2}$$

where H_1 and H_2 are the Hamiltonians for the isolated atoms. The last term V is the Coulomb interactions between all the charges in atom 1 and those in atom 2 and is treated as a perturbation in the Shrödinger equation, which can then be solve by either perturbation theory or the variational method [2]. Eisenschitz and London [6] and London [7–10] made a dipole approximation which allows only one transition state per atom, and showed that the first term in the solution of the perturbation theory vanishes for nonpolar atoms. Therefore, from the second-order perturbation theory, London obtained the VDW interaction for two isotropic neutral atoms, 1 and 2, at separation r:

$$V=-C_6/r^6 \tag{3}$$

$$C_6=\left(\frac{3\hbar}{\pi}\right)\int d\omega\,\alpha_1(i\omega)\,\alpha_2(i\omega). \tag{4}$$

Here, α_1 (iω) and α_2 (iω) represents the dynamic polarizabilities of atoms 1 and 2, respectively.

For systems involving atoms or molecules with non-zero (or excess or non-vanishing or non-negligible) permanent electric multipoles (charge, dipole moment, quadrupole moment, etc.), the VDW interaction is definitely weaker than the electrostatic or induction contributions. However, for many systems composed of neutral non-polar particles, the VDW interaction becomes the dominant force and starts to play a crucial role in the function and stability of the system. This is mainly due to the fact that the dispersion interaction is ubiquitous like the gravitational interaction, and more importantly to the fact that it depends strongly on the detailed structure or shape of the nanoscale materials [11, 12]. The VDW interaction is ubiquitous since it is originated from the quantum mechanical fluctuation of electronic density (or dynamic polarization) of any atom or molecule in the universe. In fact, this is the force responsible for the condensation and crystallization of van der Waals crystals (such as solid helium), for the structures and energetics in colloid chemistry and biology, for the formation of liquid crystalline phases in solutions, for the anomalous swelling of clay soils on addition of water, for the formation of molecular crystals, and for viral self-assembly, to name a few [1–5, 13–20]. As the size of the system decreases into the region of micro and nanotechnology, the property of material in nanoscale changes from that of macro system [21]. The variety of modern technologies, especially electronic, mechanical, chemical, and bioengineering applications, indeed demand an accurate prediction that can lead to a delicate control over nano-sized small clusters of particles or devices [22, 23]. A specific example would be the micro-machine and nano-machine. Nanocolloids is also a research field in which the VDW forces play a key role in designing and manufacturing devices, such as nanoelectromechanical systems (NEMS), low-power circuits, miniature barcodes, etc. Another example among many others is the research field of physical adsorption [24–26] of atoms or molecules on various surfaces with possible applications to micro- and nano-sensors.

From a theoretical point of view in dealing with macro or even micro-sized systems, the common understanding until very recent years has been that the estimation of long-range van der Waals force is a well-defined problem and easily calculable. On the other hand, the estimation of short-range forces is considered as computationally more challenging because it involves the many-electron problem with overlapping electronic densities that requires inevitable approximations. It should be noted here that, in principle, the estimation of VDW dispersion forces also involves collective many-body problem: among atoms and molecules or between atoms and a surface or between clusters of atoms or molecules. However, this complication of atomistic many-body problem was often considered resolved by using the Clausius-Mossotti relation [27] to estimate the effective atomic properties (atomic polarizability) from the readily measurable macroscopic properties (permittivity function) of the corresponding condensed-matter bulk system. Using this effective atomic polarizability, the dispersion interaction of an atom and a cluster of atoms, for example, has been represented by a sum of London's two-body interactions between the atom and each constituent atoms of the cluster assigned with the effective atomic polarizabilities. This approach is commonly called the pair-sum or 2-body approximation [28].

The procedure of calculating the interaction energy of macroscopic bodies by summing the pair interactions between the individual atoms or molecules of these bodies, as mentioned above, is based on the assumption of additivity of the interatomic interaction energies. This assumption of additivity is justified only within the scheme of the second order perturbation theory [2, 29, 30] since the first nonadditive contribution occurs in the third-order perturbation theory. The nonadditive correction term due to three-body (or, triple-dipole) interactions was first obtained by Axilrod, Teller, and Muto (ATM) [31–33] in 1943 using the third order perturbation theory. Since then considerable efforts have been spent to evaluate the contribution of the nonadditive corrections to the pairwise 2-body interaction term, due to three-body and even four-body interactions derived from the third- and fourth-order perturbation theory, respectively [34–38]. The common reasoning behind the reluctance to explore further the higher-order many-body contributions was the assumption that the higher-order term in the perturbation theory would be smaller than the lower-order terms. However, at the same time, a concern recognized by some researchers was that the higher-order many-body contributions might not be so simply negligible in condensed matter systems. As will be see in the next section, the number of combinations of atoms that contribute to each n-th order many-body term in the perturbation theory increases significantly as the order n increases. Therefore, even though the VDW interaction of each combination of many-atoms might become weaker as n increases, the net contribution of the n-th order term after summing over the largely increased number of combinations might not necessarily be negligibly smaller than, for example, that of the (n − 1)-th order term. The main reason, at least to my opinion, that has kept many researchers away from further estimating the actual “quantitative” contribution of higher-order many-body interaction terms whose expression can be derived from the perturbation theory is the impractically cumbersome expressions of these many-body terms, as can be seen in Refs. [34–36]. Avoiding the use of these cumbersome expressions is one of the main advantages of using the trace-CDM (TCDM) which is presented in the next section.

One of the most studied VDW systems is the inert gases. The potential energy of like pairs of inert gas atoms is quite well known empirically. However, the total potential energy of a bulk system of inert gases is not precisely equal to the sum of the atomic pair potentials. There is an extensive body of work [39–41] which shows that if accurate pair potentials are used, the inclusion of the ATM three-body VDW interaction gives a good agreement with experiment for condensed rare gas systems. For example, the triple dipole dispersion energy for solid xenon is 10 % of the total cohesive energy of xenon, with similar fractional contributions for the lighter inert gases (Ne, Ar or Kr) [39]. More significantly found is that if the ATM interaction is omitted there is a definite disagreement with experiment, which cannot be remedied by simply modifying the pair potential. This is due to the strong dependence of the ATM interaction on the relative location of the three atoms involved, that is, on the type of triangle formed by these three atoms. As material becomes denser and as its shape becomes more anisotropic, the importance of the many-body interaction terms increases.

There is another extreme theoretical approach to obtain the dispersion interaction between an atom with a substrate or a large cluster of atoms, or between two large clusters of atoms. That is to consider the substrate or the large cluster of atoms as a continuum, characterized with a dielectric tensor ε (ω), instead of recognizing it as a cluster of many individual atoms characterized with atomic polarizabilities α(ω). This continuum description of matter has an advantage over the prior-mentioned atomistic description of matter as all the many-body terms are intrinsically included. This continuum approximation method is, however, known to work well only when the distance between interacting particles is much larger than the interatomic distance of atoms within a cluster or a substrate [4, 5, 42–45]. In fact, the continuum methods are found to overestimate the many-body "screening" effect in nanoscale systems [28].

The significant improvement in accuracy achieved in recent experimental measurements of the force between nanoscale materials, especially in the force microscopy, such as atomic force microscopy (AFM), challenges for advanced calculations and thus more accurate predictions that can (1) incorporate the detailed atomistic nanostructures at the surface or edge of nanomaterials and (2) include all the nonadditive many-body interaction terms as well [46]. Because the aforementioned atomistic approach has the advantage of being sensitive to the detailed structure of the nanomaterials, many efforts have been made to find an atomistic approach that also can include "all" the many-body terms, beyond the three-body terms.

Since early 2005, the author was involved in an effort to explore better ways to estimate the van der Waals dispersion interaction accurately in nanoscale systems in collaboration with a group of enthusiastic theoretical and experimental experts. This collaborative effort led us to a series of studies using the coupled dipole method (CDM) [28, 47–52]. The focus of our original work was mostly on the accurate estimation of the van der Waals interaction between two nano-sized dielectric clusters of various shapes and relative orientations. However, the method is general and is readily applicable to other systems.

The aim of this chapter is to provide a self-contained overview of the subject of CDM. Also presented is an efficient way to execute CDM, henceforth called trace-CDM (TCDM), in order to reduce the computational burden of memory and run time, while maintaining accuracy. TCDM will allow cost-effective implementation of CDM for systems composed of large number of particles, such as those in computer simulation studies. The formulations and computational techniques are summarized in great details as some of these were omitted in the original publications due to space limit.

The outline of this chapter is as follows. The next section provides the formulation of CDM which calculates the nonretarded VDW interaction energies exactly within the dipole approximation. Also presented is the formulation of TCDM, an efficient computational way of solving CDM, which obtains accurate VDW energies without having to solve for all the eigenvalues. A few simple cases are solved analytically, as examples, to demonstrate the use of both CDM and TCDM. Section 3 concludes this chapter with a brief discussion on the importance of including all the many-body interaction terms (or at least up to the 10-th order term) and the practical advantages of using TCDM over two traditional ways of including many-body terms, the eigenvalue method of CDM and the perturbation theory.

2 Coupled Dipole Method (CDM) and Trace-CDM (TCDM) for Non-retarded VDW Interaction

The VDW attraction is truly a quantum mechanical phenomenon. That is why, as mentioned in the previous section, the mystery of VDW attractive dispersion interaction could only be unveiled by London adopting then newly established quantum mechanics theory. Quantum theory in its simplest form tells us that everywhere in space there are quantized electromagnetic radiation fields. In other words, there are photons everywhere in random motion. These photons get constantly absorbed and emitted by any particles in the system, so that induced dipole moments are formed instantaneously on the particles. The interaction energy between these instantaneously induced dipoles obtains the attractive VDW dispersion interaction energy which obeys the $1/r^6$ relationship for two atoms at separation r as shown in Eqs. (3) and (4). The final form of the VDW dispersion energy is given in terms of their atomic or molecular dynamic polarizabilities, and tends to increase rather than decrease with increasing temperature due to the increase of polarizabilites with increasing temperature [53].

Using the Schrödinger formalism, the correct free energy of the coupled electron-photon system is obtained only if both the electron and the photon remain essentially in their ground states. This implies the restriction to direct electron transitions to and from an excited state with no successive transitions through different excited states, and thereby implies that only zero or one photon of corresponding transition energy of each excited state is absorbed or emitted. Each transition may be represented by a single excitation of a quantum mechanical harmonic oscillator. London simplified the system by assuming that only one excited state is available for each harmonic oscillator, and thus the interacting ground-state atoms can be represented by equal number of interacting harmonic oscillators whose characteristic frequencies are equal to the electronic excitation energies. This is the point where the quantum mechanical formulation of London makes a connection to the classical Lorentz harmonic oscillator model of atoms (frequently also called Drude model) which has been used to explain the interaction between electromagnetic fields and matter since 1900 [54, 55].

It should be noted that the Schrödinger formalism adopted by London is nonrelativistic, and the many-electron Schrödinger equation assumes static electromagnetic interaction potentials between all electrons. There is an exact quantum mechanical treatment, the quantum electrodynamics (QED) procedure, of the dispersion interaction which involves quantization of both matter and electromagnetic fields (or photons). The full quantum mechanical analysis is far too complicated and would not add much to our current purpose. The conclusion in non-relativistic regime and thus in the non-retarded VDW interaction, which is the subject of interest in this chapter, remains unaltered.

In practice, to calculate the VDW interaction energies, certainly among condensed matter scientists and engineers, the oscillator model has been strongly favored due to its simplicity and to the fact that they already have a readily available tool to estimate the atomistic polarizability from the macroscopic dielectric constant using the Clausius-Mossotti relation. In 1963, McLachlan [56, 57] derived the VDW dispersion interaction starting from the Drude model of atoms. In CDM, following McLachlan's approach, the oscillator model is employed to derive the nonretarded VDW interaction energy of a cluster of atoms or between clusters of atoms. The general form of the dynamic atomic polarizability of a Drude harmonic oscillator is:

$$\alpha(\omega) = \left(\frac{e^2}{m}\right)\sum_k \frac{1}{\left(\omega_{ok}^2 - \omega^2\right)} = \sum_k \frac{\alpha_{ok}}{\left(1 - \frac{\omega^2}{\omega_{ok}^2}\right)} \tag{5}$$

Here ω_{0k} and α_{0k} is the characteristic frequency and static polarizability of the k-th electron transition in the atomic states. For the simplest Drude atomic model, where an atom is represented with one characteristic frequency (ω_0) and the isotropic static polarizability (α_0) as assumed by London, the dynamic atomic polarizability becomes:

$$\alpha(\omega) = \frac{\alpha_o}{\left(1 - \frac{\omega^2}{\omega_o^2}\right)} \tag{6}$$

Substituting Eq. (6) to (4) yields, after the integration over frequency, another form of London's formula for the VDW interaction energy of two identical atoms at separation r:

$$V = -\frac{3}{4}\hbar\omega_0\frac{\alpha_0^2}{r^6} \tag{7}$$

Before going any further, it should be noted here that the London's simple oscillator model has been generalized [2, 29, 30] by allowing more than one electronic transition states per atom. With this generalized oscillator model, there appear additional nonvanishing higher-order terms in the second order perturbation theory for two isolated atoms which correspond to the instantaneous dipole-quadrupole, quadrupole-quadrupole interaction, etc. (see Eqs. 36 and 37 in Ref. [2]) Although these higher-order multipole interaction terms are interesting on their own, they are out of scope of this chapter. Here, we will focus on the dispersion interaction due to the instantaneous fluctuating dipole moments of ground state atoms as adopted in London's work.

Now, using the harmonic oscillator model in Eq. (6) requires atomic values of α_0 and ω_0. Derived from the continuum theory, the Clausius-Mossotti relation connects the macroscopic matter property to the "effectively screened" microscopic property of the composing atoms [27]

$$\frac{\varepsilon(i\omega)-1}{\varepsilon(i\omega)+1}=\frac{4\pi}{3}\rho\alpha(i\omega) \tag{8}$$

Thus, by knowing the permittivity function for a single resonant peak, atomistic values for $\rho\alpha_0$ and ω_0 can be calculated, where ρ is the bulk density of the material. More details on how to use this equation to obtain atomic values from experimental data and some typical atomic values can be found in Appendix D of Ref. [51]. The validity of using the Clausius-Mossotti relation, which after all is derived from the continuum model of bulk material, in estimating the atomic properties in nanoscale materials is still an open question. As the size of clusters of atoms becomes smaller, the finite-size effects such as discrete boundary conditions become evident. Therefore, the bulk properties such as the dielectric constant or bulk density are not well defined. Although it is very important and interesting, this subject is out of scope of this chapter. Since the CDM formulation is independent from how one estimates the atomic polarizability and the characteristic frequency, we proceed without digressing. Following formulations and calculations of CDM and TCDM adopt the Clausius-Mossotti relation.

The CDM is a self-consistent method that is intrinsically atomistic and yet includes all many-body interaction terms, both of which are the characteristics of the very method, as described in Sect. 1, that can best estimate the VDW interactions among nanoscale materials. The detailed formulation is as follows [28, 49–52].

2.1 Formulation

Let us consider a system of two clusters of atoms of nano-size and of arbitrary shape as an example. By definition, the VDW interaction between two clusters A and B (with number of atoms N and N′, respectively) is the change in total energy of the system with two clusters at finite separation relative to that of the system with two clusters at infinite separation. Therefore, using CDM, one may first calculate the total energy ($V_{N+N'}$) of a system of N + N′ atoms, the total energy (V_N) of a system of N atoms, and the total energy ($V_{N'}$) of the system of (N′) atoms separately. And then, the VDW interaction energy of the system is simply obtained from subtracting the self-energy of individual clusters from the total energy of the composite system:

$$V_{vdw} = V_{N+N'} - V_N - V_{N'} \tag{9}$$

To demonstrate the CDM formulation in detail, let us start with a system containing only one cluster A of N atoms. An arbitrary atom i in the cluster will have an instantaneous dipole moment (characterized by the dynamic atomic polarizability) induced by the net local instantaneous electric field, $\vec{E}(\vec{x}_i)$:

$$\vec{p}_i = \overset{\leftrightarrow}{\alpha}_i \cdot \vec{E}(\vec{x}_i) \tag{10}$$

where the atomic polarizability is written in its general form of a tensor, which is assumed isotropic in Eqs. (5) and (6). $\vec{x}_i$ is the position vector of the atom i. The local instantaneous electric field at $\vec{x}_i$, in the absence of any externally applied field, results from the vector sum of instantaneous electric fields due to instantaneously induced dipole moments of all other atoms in the system:

$$\vec{E}(\vec{x}_i) = \sum_{\substack{j=1 \\ j \neq i}}^{N} \overset{\leftrightarrow}{T}_{ij} \cdot \vec{p}_j \tag{11}$$

where, $\overset{\leftrightarrow}{T}_{ij}$ is the usual 3-dimensional static-dipole-interaction tensor (or, a 3 × 3 matrix):

$$\overset{\leftrightarrow}{T}_{ij} \equiv \begin{cases} \left(\dfrac{3\hat{n}_{ij}\hat{n}_{ij} - \overset{\leftrightarrow}{I}}{r_{ij}^3} \right) & \text{for } i \neq j \\ 0 & \text{for } i = j \end{cases}. \tag{12}$$

Here, $\hat{n}_{ij} = \vec{r}_{ij} / \left| \vec{r}_{ij} \right|$ is the unit normal vector between atoms i and j, and $\overset{\leftrightarrow}{I}$ is the 3-dimensional identity tensor. Substituting Eq. (11) into Eq. (10), one obtains a set of self-consistent equations for the dipoles, one for each atom in the system:

$$\vec{p}_i - \sum_{\substack{j=1 \\ j \neq i}}^{N} \overset{\leftrightarrow}{\alpha}_i \cdot \overset{\leftrightarrow}{T}_{ij} \cdot \vec{p}_j = 0 \tag{13}$$

Note here that the indices i and j indicate the atoms, not the vector components (e.g. p_x, p_y, p_z,, etc.). The scalar product notation assumes the usual dot-product operation between vectors and tensors. The synchronizations of the dynamic group talk between ever-fluctuating atomic polarization (or, instantaneously responding dipole moment) of N atoms in the system lead to 3N normal modes, where the factor 3 originates from the three-dimensionality of atomic structure.[1]

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[1] Despite the same notation adopted, the static-dipole-interaction tensor shown in Eq. (12) of this chapter has a different definition from the T-matrix used in Eq. (2) in Ref. [49], where the

Assuming now the isotropic atomic polarizability of Lorentz oscillator model (Eq. 6), one obtains,

$$\vec{p}_i - \frac{\alpha_{0i}}{\left(1 - \frac{\omega^2}{\omega_{0i}^2}\right)} \sum_{\substack{j=1 \\ j \neq i}}^{N} \overset{\leftrightarrow}{T}_{ij} \cdot \vec{p}_j = 0. \tag{14}$$

Rearranging terms, one obtains,

$$\vec{p}_i \left(1 - \frac{\omega^2}{\omega_{0i}^2}\right) - \alpha_{0i} \sum_{\substack{j=1 \\ j \neq i}}^{N} \overset{\leftrightarrow}{T}_{ij} \cdot \vec{p}_j = 0 \tag{15}$$

One then arrives at the formation of an eigenvalue problem,

$$\vec{p}_i - \alpha_{0i} \sum_{\substack{j=1 \\ j \neq i}}^{N} \overset{\leftrightarrow}{T}_{ij} \cdot \vec{p}_j = \left(\frac{\omega}{\omega_{0i}}\right)^2 \vec{p}_i \tag{16}$$

For a system composed of identical atoms (just to simplify the formulation), $\omega_{0\mathrm{i}}$ and $\alpha_{0\mathrm{i}}$ is simply replaced by ω_0 and α_0, respectively, and one may rewrite Eq. (16) as a matrix form to obtain

$$\left(\overset{\leftrightarrow}{I} + \overset{\leftrightarrow}{Q}\right) \cdot \vec{\mathrm{P}} = \left(\frac{\omega}{\omega_0}\right)^2 \vec{\mathrm{P}}. \tag{17}$$

Here, $\vec{\mathrm{P}}$ is now a 3N column matrix (x,y,z-components of each N dipoles), $\overset{\leftrightarrow}{I}$ is a 3N × 3N identity matrix, and $\overset{\leftrightarrow}{Q} \equiv -\alpha_0 \overset{\leftrightarrow}{T}$ is a 3N × 3N square matrix for a system composed of identical atoms. Standard linear algebra algorithms, such as the free software LAPACK (Linear Algebra PACKage) [58] or ScaLAPACK (Scalable LAPACK) [59], can be used to solve this eigenvalue problem by diagonalization of the matrix $\left(\overset{\leftrightarrow}{I} + \overset{\leftrightarrow}{Q}\right)$. There are 3N eigenvalues ($(\omega_\mathrm{k}/\omega_0)^2$) with the integer index k runs from 1 to 3N obtained in this eigenvalue problem, which can then provide the 3N normal mode frequencies (ω_k) in units of ω_0. Since each normal mode frequency contributes a ground state energy of $\hbar\omega_k/2$ (or at finite temperature,

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(Footnote 1 continued)
dimensionless T-matrix is defined as $\overset{\leftrightarrow}{T}_{ij} = -\alpha_i(\omega)\left(3\hat{n}_{ij}\hat{n}_{ij} - \overset{\leftrightarrow}{I}\right)/r_{ij}^3$ for i ≠ j. Note that this dimensionless T-matrix adopted in Ref. [49] corresponds to the Q-matrix defined in Eq. (17) of this chapter. Accordingly, Eq. (1) in Ref. [49] should be corrected as $\vec{p}_i + \sum_{\substack{j=1 \\ j \neq i}}^{N} \overset{\leftrightarrow}{T}_{ij} \cdot \vec{p}_j = 0$, which then becomes equivalent to Eq. (13) of this chapter as it should be.

$(\hbar\omega_k/2)\coth(\hbar\omega_k/2kT)$ [60][2]), one finds the total energy of a system composed of N-Lorentz oscillators from

$$V_N = \frac{\hbar}{2}\sum_{k=1}^{3N}\omega_k \tag{18}$$

Therefore, by solving 3N linear equations self-consistently, CDM automatically provides the contributions of all many-body interactions. Note that one can also calculate the 3N eigenvectors corresponding to these eigenvalues, which corresponds to the dynamic polarizability of the cluster of atoms, i.e., the dipole moments of the system of atoms as a whole. It should be noted as well that the assumption of isotropic atomic polarizability made here is purely for computational convenience and the general form of anisotropic atomic polarizability can be adopted in CDM.

Now, let us return to our original problem of a system of two clusters, A and B, composed of N and N′ identical atoms, respectively. One obvious way to obtain the VDW interaction energy between two clusters is to strictly follow the method described above and solve for 3N eigenvalues of the cluster A. And then use the same procedure to solve for 3N′ eigenvalues of the cluster B, and then again use the same procedure to solve for 3(N + N′) eigenvalues for the composite system of (N + N′)-atom system of two clusters A and B. That is, one would diagonalize the matrix in the eigenvalue problem (Eq. (17)) to solve for all eigenvalues, and sum up the zero-point energy contributions of each and every eigenmode as shown in Eq. (18) to obtain the total energy of each cluster (V_N and $V_{N'}$, separately) and that of the total system ($V_{N+N'}$) [49–52]. The final step is to use Eq. (9) to obtain V_{vdw}. If one were to estimate the VDW energy of a system composed of many (N + N′, for example) atoms, instead of the VDW energy between two clusters of atoms, one simply needs to replace V_N and $V_{N'}$ in Eq. (9) by a sum of self-energies of individual atoms $3N\hbar\omega_0/2$ and $3N'\hbar\omega_0/2$, respectively. In Eq. (9) the subtraction of self-energies of individual atoms were not explicitly shown since the atomic self-energy terms from single-cluster systems A and B cancel those from the whole system (A + B). In other words, while the total energies in Eq. (9), V_N, $V_{N'}$ and $V_{N+N'}$, include the self-energies of composing atoms, the final VDW interaction energy V_{vdw} is free from the self-energies of composing atoms or clusters. The VDW interaction energy obtained this way includes all the higher-order many-body interaction terms, and thus is exact within dipole approximation. This method of solving CDM has been successfully implemented in various quantum chemistry calculations based on density-functional theory (DFT) [13, 61–63] and computer simulations [64]. In principle, one may extend this method to include the higher-order multipole interactions by including

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[2] Lifshitz EM (1956) The theory of molecular attractive forces between solids. Sov. Phys. JETP 2:73-83; The dispersion force can be treated for finite temperature by substituting $\frac{\hbar\omega}{2}$ by $\frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/kT}-1} = \frac{\hbar\omega}{2}\coth\left(\frac{\hbar\omega}{2kT}\right)$ to account for the thermal excitation of the modes.

more characteristic frequencies than one per each harmonic oscillator [2] as mentioned in the introduction.

In a quantum chemistry study based on DFT with CDM implemented [63], it is observed that the computational cost of calculating the many-body VDW interactions using CDM is negligible compared to the underlying electronic structure calculation. It should be, however, noted here that these quantum chemistry calculations are done for systems composed of very small number of atoms (less than 200). On the other hand, computational material scientists [64] are making an effort to implement CDM into the Massively Parallel Monte Carlo (MPMC). MPMC is an open-source computer code [65] developed to study the interactions of gas phase sorbates and various metal-organic materials (MOF). As the number of particle N increases, the increasing size of matrices renders the matrix diagonalization in the eigenvalue method of CDM impractical. The bottle-neck of this challenge of implementing the CDM for large size systems comes from both memory size and run time since these grow as N^2 and N^3, respectively [28]. To circumvent the challenge of memory size, many studies involving large number of particles such as computer simulation studies in Ref. [64] calculates the many-body VDW interaction by solving the eigenvalue problem iteratively. Another way to meet this challenge of memory size is to parallelize the computer code so that diagonalization of large-size matrix can be performed. Successfully parallelized codes of CDM have been demonstrated to study systems of large (unlimited, in principle) number of particles [28, 64]. The challenge in the computational run time of using the eigenvalue method of CDM for a large system remains unresolved thus far.

There is, however, a way to circumvent both of these challenges. This procedure, which will be called as Trace-CDM (TCDM) from here on, does not require matrix diagonalization and allows one to obtain the VDW interaction energy V_{vdw} with much better efficiency and still with great accuracy. TCDM simply uses the fact that the trace of a square matrix is equal to the sum of its eigenvalues [37, 66, 67]. According to this, once the eigenvalue problem is written in its matrix form, the sum of all the eigenvalues equals the trace of the square matrix of the eigenvalue problem. This would be a great alternative way for those who are not interested in obtaining the individual eigenvalues, but just the sum of those as shown in Eq. (18). Unfortunately for those, however, the eigenvalue problem shown in Eq. (17) has eigenvalues as $\left(\omega_k^2/\omega_0^2\right)$, not (ω_k/ω_0). Therefore, the trace of the square matrix $\left(\overleftrightarrow{I}+\overleftrightarrow{Q}\right)$ in Eq. (17) is equal to $\sum_{k=1}^{3N}\left(\omega_k^2/\omega_0^2\right)$, not to $\sum_{k=1}^{3N}(\omega_k/\omega_0)$. Only if one could set up the eigenvalue problem so that the eigenvalues are not $\left(\omega_k^2/\omega_0^2\right)$, but (ω_k/ω_0), the VDW interaction energy of the system can be obtained straightforwardly according to Eq. (18). For that, the eigenvalue problem in matrix form in Eq. (17) may be rewritten as:

$$\left(\overleftrightarrow{I}+\overleftrightarrow{Q}\right)^{1/2}\cdot\vec{P}=\left(\frac{\omega}{\omega_0}\right)\vec{P} \tag{19}$$

and from this, one obtains the total VDW energy of the system of N particles:

$$Tr\left(\overset{\leftrightarrow}{I}+\overset{\leftrightarrow}{Q}\right)^{1/2}=\sum_{k=1}^{3N}\left(\frac{\omega_k}{\omega_0}\right)=V_N/(\hbar\omega_0/2), \tag{20}$$

where Tr denotes the invariant trace, the sum of eigenvalues. Finding the square root of a matrix, $\left(\overset{\leftrightarrow}{I}+\overset{\leftrightarrow}{Q}\right)^{1/2}$, however, is not an easy task and requires expensive linear algebra computations which would not offer any advantage over solving for all the eigenvalues of the original matrix, $\left(\overset{\leftrightarrow}{I}+\overset{\leftrightarrow}{Q}\right)$, as would have been done in the eigenvalue method of CDM.

To meet our original purpose of finding the memory-efficient and cost-effective way to solve CDM, let us take a detour route similar to the one taken in the perturbation theory. In short, noticing the form of the matrix in Eq. (20), let us expand it in the power series in terms of $\overset{\leftrightarrow}{Q}^n$ using the usual binomial expansion as follows [37, 67]:

$$\left(\overset{\leftrightarrow}{I}+\overset{\leftrightarrow}{Q}\right)^{1/2}=\sum_{n=0}^{\infty}c_n\overset{\leftrightarrow}{Q}^n. \tag{21}$$

Here c_n are the coefficients found in the following binomial expansion

$$(1+y)^{1/2}=\sum_{n=0}^{\infty}c_n y^n \tag{22}$$

$$\begin{aligned} c_0 &= 1 \\ c_n &= c_{n-1}\left(\frac{3}{2n}-1\right) \qquad \text{for n} \neq 0 \end{aligned}$$

Then, using the properties of trace in linear algebra, the trace of the square-root of the matrix in Eq. (20) may be represented as a sum of traces of the multiples of the matrix ($\overset{\leftrightarrow}{Q}^n$) as follows:

$$Tr\left[\left(\overset{\leftrightarrow}{I}+\overset{\leftrightarrow}{Q}\right)^{1/2}\right]=Tr\left[\sum_{n=0}^{\infty}c_n\overset{\leftrightarrow}{Q}^n\right]=\sum_{n=0}^{\infty}c_n Tr\left[\overset{\leftrightarrow}{Q}^n\right] \tag{23}$$

Now, the total VDW interaction energy of the system of a cluster of N atoms is,

$$V_N=\frac{\hbar\omega_0}{2}Tr\left[\left(\overset{\leftrightarrow}{I}+\overset{\leftrightarrow}{Q}\right)^{1/2}\right]=\frac{\hbar\omega_0}{2}\sum_{n=0}^{\infty}c_n Tr\left[\overset{\leftrightarrow}{Q}^n\right]\equiv\frac{\hbar\omega_0}{2}\sum_{n=0}^{\infty}W_N^{(n)} \tag{24}$$

Obtaining the traces of $\overleftrightarrow{Q}^{n}$ is not much of a computational burden. As discussed later in this section, each n-th order term in this power series expansion indeed corresponds to the n-th order term in the perturbation theory. Also, according to the exact CDM calculations done in Ref. [49], including up to 10-th order terms in this power series expansion reproduces the exact CDM result for varying shapes and orientations of nanomaterials within much less than 1 % error (see Table 1). Figure 2 of Ref. [49] is reproduced in Fig. 1. The fractional percent energy is defined as

$$\text{Fractional \% Energy of order M} = \frac{\frac{\hbar\omega_0}{2}\sum\limits_{n=0}^{M} W_N^{(n)}}{V_N} \times 100 = \frac{\sum\limits_{n=0}^{M} W_N^{(n)}}{\sum\limits_{n=0}^{\infty} W_N^{(n)}} \times 100 \qquad (25)$$

Also, the numeric values of the fractional percent energy are listed in Table 1 up to the interaction order M = 15. Same symbols as adopted in Fig. 1 are used in Table 1 to indicate the corresponding configuration (orientations and types) of clusters to the ones shown in the inset of Fig. 1.

Therefore, TCDM provides a great alternative way for those who are interested only in obtaining the final VDW interaction energies (V_{vdw}), and not in obtaining the individual eigenvalues (ω_k′s) and/or the corresponding eigenvectors. Returning back to our original problem of a system of two clusters A and B, composed of N and N′ identical atoms, respectively, to solve it with TCDM one starts with the self-consistent equations for '*all*' atoms in the system (N + N′) that can be expressed in matrix form

Table 1 Numerical values of the fractional percent energy of order M to the total VDW interaction energy as a function of the highest-order (M) of many-body terms included. Each symbol indicates the cluster configuration shown in the *inset* of Fig. 1

M	Decamer △	Decamer ●	Cubes ◇
2	48.66	93.93	99.33
3	65.96	77.22	95.29
4	81.93	92.87	101.03
5	89.64	94.37	99.41
6	94.42	97.37	100.23
7	96.94	98.44	99.87
8	98.36	99.19	100.07
9	99.12	99.56	99.96
10	99.53	99.77	100.03
11	99.75	99.87	99.98
12	99.87	99.93	100.02
13	99.93	99.96	99.99
14	99.96	99.98	100.01
15	99.98	99.99	99.99

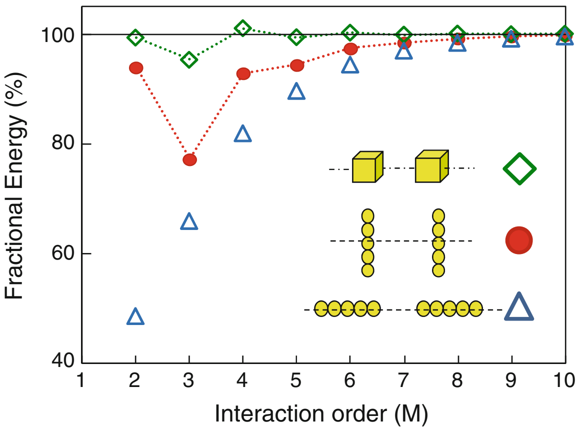


Fig. 1 Fraction of total VDW interaction energy as a function of the highest-order (M) of many-body terms included. Triangles (*circles*) correspond to the VDW interaction between two decamers at separation r/a = 50, where a is the separation between nearest atoms in the linear chain. Diamonds corresponds to the VDW interaction between two 27-atom cubic clusters at r/a = 10. Atoms in each cubic cluster are arranged in a simple cubic lattice structure with lattice constant a. The *dashed lines* are drawn to guide the eye. Refer to Ref. [49] for more details

$$\overleftrightarrow{\Omega} \cdot \vec{P} = \lambda^2 \vec{P}, \tag{26}$$

where the eigenvalues λ^2 of the square matrix

$$\overleftrightarrow{\Omega} = \begin{pmatrix} \overleftrightarrow{I} + \overleftrightarrow{Q} & \overleftrightarrow{M} \\ \overleftrightarrow{M}' & \overleftrightarrow{I}' + \overleftrightarrow{Q}' \end{pmatrix} \tag{27}$$

are the squared eigen frequencies (i.e.,$\lambda^2 = (\omega/\omega_0)^2$) of the composite system A + B. Here, $\overleftrightarrow{Q}$ denotes a 3N × 3N symmetric, traceless matrix, made of dimensionless dipole tensors connecting two atoms within cluster A and $\overleftrightarrow{I}$ is the 3N × 3N identity matrix, as already have been used in Eq. (19) for the system of N particles. $\overleftrightarrow{Q}'$ and $\overleftrightarrow{I}'$ are the corresponding matrices for the N′ atoms within cluster B. $\overleftrightarrow{M}$ is a 3N × 3N′ matrix representing the dipole interaction tensors connecting one atom in A to another atom in B. $\overleftrightarrow{M}'$ is the transpose matrix (a 3N′ × 3N matrix) of matrix $\overleftrightarrow{M}$ representing the dipole tensor connecting one atom in B to another atom in A. The eigenvalue problems of $\overleftrightarrow{I} + \overleftrightarrow{Q}$ and $\overleftrightarrow{I}' + \overleftrightarrow{Q}'$ correspond to that of each cluster A and B (see Eq. 19), respectively. As mentioned before, in TCDM, the exact non-retarded VDW dispersion energy from each eigenvalue problem is obtained by taking the trace of the square matrices:

$$W_{vdw} = Tr\left[\overleftrightarrow{\Omega}^{1/2}\right] - Tr\left[\left(\overleftrightarrow{I} + \overleftrightarrow{Q}\right)^{1/2}\right] - Tr\left[\left(\overleftrightarrow{I}' + \overleftrightarrow{Q}'\right)^{1/2}\right]. \tag{28}$$

This equation is essentially identical with Eq. (9), except that W_{vdw} is now a dimensionless VDW energy and is equal to $V_{vdw}/(\hbar\omega_0/2)$ when all the atoms in the system are identical.

The second term in the right hand side of Eq. (28) is the matrix for a system of a cluster (A) of N particles, and has already been expanded earlier in Eq. (23). Similarly, the third term in the right hand side of Eq. (28) may be expanded as:

$$Tr\left[\left(\overleftrightarrow{I}' + \overleftrightarrow{Q}'\right)^{1/2}\right] = \sum_{n=0}^{\infty} c_n Tr\left[\overleftrightarrow{Q}'^{n}\right]. \tag{29}$$

The power law expansion of the first term in the right hand side of Eq. (28) can also be done as follows:

$$Tr\left[\overleftrightarrow{\Omega}^{1/2}\right] = Tr\left[\left\{\begin{pmatrix} \overleftrightarrow{I} & 0 \\ 0 & \overleftrightarrow{I}' \end{pmatrix} + \begin{pmatrix} \overleftrightarrow{Q} & \overleftrightarrow{M} \\ \overleftrightarrow{M}' & \overleftrightarrow{Q}' \end{pmatrix}\right\}^{1/2}\right] = \sum_{n=0}^{\infty} c_n Tr\left[\begin{pmatrix} \overleftrightarrow{Q} & \overleftrightarrow{M} \\ \overleftrightarrow{M}' & \overleftrightarrow{Q}' \end{pmatrix}^{n}\right] \tag{30}$$

Consequently, the dimensionless total interaction energy in Eq. (28) can now be written as a sum of all $\{W^{(n)}\}$ contributions, which again is equivalent to Eq. (9) in units of $\hbar\omega_0/2$:

$$W_{vdw} = \sum_{n=0}^{\infty} W^{(n)} \tag{31}$$

where, $W^{(n)}$ is the n-th order contribution to the dispersion interaction:

$$W^{(n)} = c_n\left\{Tr\left[\begin{pmatrix} \overleftrightarrow{Q} & \overleftrightarrow{M} \\ \overleftrightarrow{M}' & \overleftrightarrow{Q}' \end{pmatrix}^{n}\right] - Tr\left[\overleftrightarrow{Q}^{n}\right] - Tr\left[\left(\overleftrightarrow{Q}'\right)^{n}\right]\right\} \tag{32}$$

Incidentally, since the eigenvalues of $\overleftrightarrow{\Omega}$ and $\overleftrightarrow{I} + \overleftrightarrow{Q}$ (or $\overleftrightarrow{I}' + \overleftrightarrow{Q}'$) are necessarily of the form $\lambda_i^2 = 1 + x_i$ and $\lambda_{0i}^2 = 1 + x_{0i}$, respectively, these traces are readily expressed in terms of x_i and x_{0i}. Therefore we obtain yet another form of the general n-th order contribution to the dispersion interaction:

$$W^{(n)} = c_n\left[\sum_{i=1}^{3(N+N')} (x_i)^n - \sum_{\substack{j=1 \\ j\in A}}^{3N} \left(x_{0j}\right)^n - \sum_{\substack{k=1 \\ k\in B}}^{3N'} (x_{0k})^n\right] \tag{33}$$

This expansion is the equivalent power-series (or perturbation) expansion in terms of $\rho\alpha_0$, as demonstrated in Ref. [49] using the eigenvalue method of the exact CDM, to which all $\overset{\leftrightarrow}{M}$ and $\overset{\leftrightarrow}{Q}$ matrices are proportional.

In Eq. (32), since the power series expansion is in matrix form, it is easier to identify where each n-th order many-body term originates from. For example, $W^{(0)} = 0$ due to the cancellation of atomic zero-point energies; $W^{(1)} = 0$ due to the tracelessness of Q matrices for a neutral non-polar system; $W^{(2)} = 2c_2\,\mathrm{Tr}\,(MM')$ due to the pairwise interaction terms with one atom in A and another in B; $W^{(3)} = 3c_3\,\mathrm{Tr}\,(QMM' + Q'M'M)$ due to the triplets with one atom in A and two atoms in B or vice versa; $W^{(4)} = 4c_4\,\mathrm{Tr}(QQMM' + Q'Q'MM' + QMQ'M' + M'MM'M/2)$, etc. A quick review of linear algebra reveals that the matrix in a trace of a product can be switched allowing tr(AB) = tr(BA). Equivalently, the trace is invariant under cyclic permutations, i.e., tr(ABCD) = tr(BCDA) = tr(CDAB) = tr(DABC). This gives the factors of 2 and 3 in the above expressions of $W^{(2)}$ and $W^{(3)}$, respectively. In Fig. 2, schematic diagrams are drawn to aid the intuitive understanding of the n-th order many-body interaction contributions.

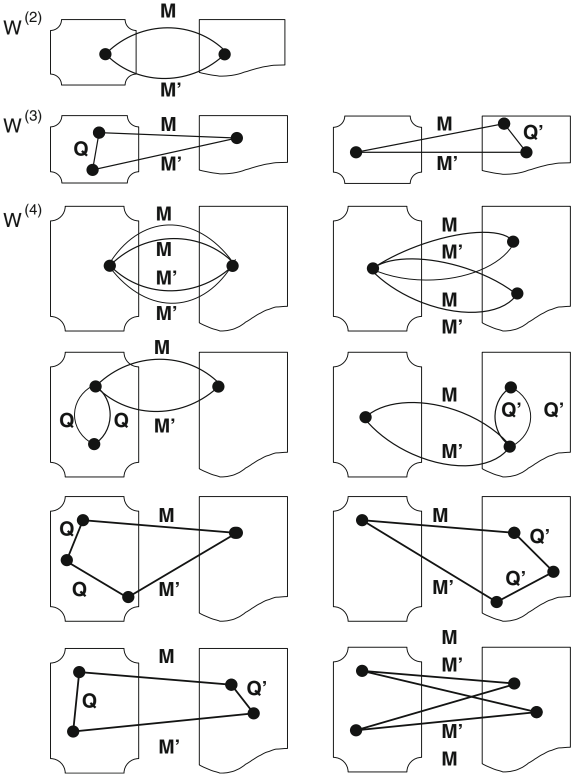


Fig. 2 Schematic diagrams of the n-th order many-body interaction contributions

To gain a solid understanding of how the TCDM works and what makes it so efficient, we will lay out four examples of calculating the VDW interaction energies for a couple of simple systems using both ways: (1) The eigenvalue method of exact CDM which adds all the eigenvalues obtained from diagonalizing the square matrix in the eigenvalue problem, and (2) the alternative way of TCDM which calculates the trace of the square-root of the matrix by expanding it in binomial power series. We will show that these two methods give same results as they should.

2.2 Example 1: Calculation of the VDW Interaction Energy of a Pair of Identical Non-polar Atoms Using TCDM

Let us consider a pair of identical non-polar atoms at a distance of r (Fig. 3). This problem is the simplest case and the eigenvalue problem becomes:

$$\begin{pmatrix} 1 & 0 & 0 & \gamma & 0 & 0 \\ 0 & 1 & 0 & 0 & \gamma & 0 \\ 0 & 0 & 1 & 0 & 0 & -2\gamma \\ \gamma & 0 & 0 & 1 & 0 & 0 \\ 0 & \gamma & 0 & 0 & 1 & 0 \\ 0 & 0 & -2\gamma & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} p_{1x} \\ p_{1y} \\ p_{1z} \\ p_{2x} \\ p_{2y} \\ p_{2z} \end{pmatrix} = \left(\frac{\omega}{\omega_0}\right)^2 \begin{pmatrix} p_{1x} \\ p_{1y} \\ p_{1z} \\ p_{2x} \\ p_{2y} \\ p_{2z} \end{pmatrix} \tag{34}$$

where, $\gamma = \alpha_0/r^3$.

To remain closely related to the general formulations discussed previously for the VDW interactions between two clusters of atoms, purely for the purpose of demonstration, let us assume that these atoms belong to two different clusters A and B. Then, comparing Eq. (34) to Eqs. (26) and (27), one obtains $\overset{\leftrightarrow}{Q} = \overset{\leftrightarrow}{Q}' = 0$ and

$$\overset{\leftrightarrow}{M} = \overset{\leftrightarrow}{M}' = \begin{pmatrix} \gamma & 0 & 0 \\ 0 & \gamma & 0 \\ 0 & 0 & -2\gamma \end{pmatrix}. \tag{35}$$

From Eq. (32), then, one obtains the n-th order contribution to the dispersion interaction:

$$W^{(n)} = c_n Tr\left\{ \begin{pmatrix} 0 & \overset{\leftrightarrow}{M} \\ \overset{\leftrightarrow}{M}' & 0 \end{pmatrix}^n \right\}. \tag{36}$$

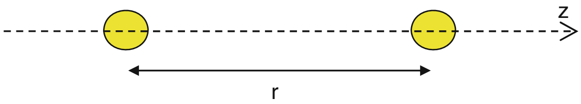


Fig. 3 A pair of identical non-polar atoms at separation r

Note that, alternatively, one could have considered this problem as a cluster of two atoms, instead of two clusters composed of one atom each. In that case, the eigenvalue problem of Eq. (34) corresponds to Eq. (19) with

$$\overset{\leftrightarrow}{Q} = \begin{pmatrix} 0 & \overset{\leftrightarrow}{M} \\ \overset{\leftrightarrow}{M}' & 0 \end{pmatrix} \tag{37}$$

and thus regaining Eq. (36) from Eq. (23). Both perspectives of the same physical system are of course equivalent.

As stated earlier, both $W^{(0)}$ and $W^{(1)}$ are zero due to the cancellation of self-energies of each atom and the tracelessness of Q matrix, respectively. When n = 2, $c_2 = -1/8$, and

$$\begin{aligned} Tr\left\{ \begin{pmatrix} 0 & \overset{\leftrightarrow}{M} \\ \overset{\leftrightarrow}{M}' & 0 \end{pmatrix} \begin{pmatrix} 0 & \overset{\leftrightarrow}{M} \\ \overset{\leftrightarrow}{M}' & 0 \end{pmatrix} \right\} &= Tr\begin{pmatrix} \overset{\leftrightarrow}{M}\overset{\leftrightarrow}{M}' & 0 \\ 0 & \overset{\leftrightarrow}{M}'\overset{\leftrightarrow}{M} \end{pmatrix} = Tr\left[\overset{\leftrightarrow}{M}\overset{\leftrightarrow}{M}' + \overset{\leftrightarrow}{M}'\overset{\leftrightarrow}{M}\right] \\ &= 2\,Tr\left[\overset{\leftrightarrow}{M}\overset{\leftrightarrow}{M}\right] \end{aligned} \tag{38}$$

The last step is taken using $M = M'$ since the two atoms are identical. Also, from Eq. (35), $Tr(MM) = 6\gamma^2 = 6(\alpha_0/r^3)^2$. Consequently, one obtains the first surviving term (n = 2) in the many-body power series expansion,

$$V_{vdw}^{(2)} = \left(\frac{1}{2}\hbar\omega_0\right) W^{(2)} = \left(\frac{1}{2}\hbar\omega_0\right)\left(-\frac{1}{8}\right)(2)\left(6\frac{\alpha_0^2}{r^6}\right) = -\frac{3}{4}\hbar\omega_0\frac{\alpha_0^2}{r^6} \tag{39}$$

Including only till the second-order term, we now recover the London's formula, Eq. (7), for two identical non-polar atoms at separation r. Let us further explore the higher-order terms. Because all the diagonal elements are zero in the matrix in Eq. (36), the trace of the n-th power of the matrix is zero for all odd n. Therefore, the next non-zero term is when n = 4, $c_4 = -5/128$ which gives

$$\begin{aligned} W^{(4)} &= c_4 Tr\left\{ \begin{pmatrix} 0 & \overset{\leftrightarrow}{M} \\ \overset{\leftrightarrow}{M}' & 0 \end{pmatrix}^4 \right\} = c_4 Tr\begin{bmatrix} \overset{\leftrightarrow}{M}\overset{\leftrightarrow}{M}'\overset{\leftrightarrow}{M}\overset{\leftrightarrow}{M}' & 0 \\ 0 & \overset{\leftrightarrow}{M}'\overset{\leftrightarrow}{M}\overset{\leftrightarrow}{M}'\overset{\leftrightarrow}{M} \end{bmatrix} \\ &= 2c_4 Tr\left[\overset{\leftrightarrow}{M}\overset{\leftrightarrow}{M}\overset{\leftrightarrow}{M}\overset{\leftrightarrow}{M}\right] = 36c_4\left(\frac{\alpha_0}{r^3}\right)^4 \end{aligned} \tag{40}$$

Or, the 4-th order VDW interaction term is obtained as

$$V_{vdw}^{(4)} = \left(\frac{1}{2}\hbar\omega_0\right) W^{(4)} = -\frac{45}{64}\hbar\omega_0\frac{\alpha_0^4}{r^{12}}. \tag{41}$$

Here, note that the power expansion coefficient c_n is always a negative number for even n due to the $(-1)^{n-1}$ factor in it. On the other hand, $Tr[M^n] = \gamma^n\,[1 + 1 + (-2)^n]$ is always positive for even n. Therefore, one can conclude that all the non-zero contribution of $W^{(n)}$ is negative. Therefore, including higher-order terms in the VDW interaction between two atoms increases the attraction. Note that this next higher order term of n = 4 in the VDW interaction of two atoms also shows up as one of the 4-body interaction terms in the VDW interaction between two clusters of many atoms (see $W^{(4)}$ in Fig. 2).

It should be noted that the n-th order contribution of Eqs. (32) and (33) in the “many-body” power series expansion of Eq. (31) is not exactly the same as the “n-body” interaction. This example of VDW interaction between “two” atoms (therefore, two-body) demonstrates that the power expansion always is an infinite order expansion [68]. The reasoning behind the conventional use of London’s formula for the VDW interaction energy for the two-atom system is based on the usual assumption of perturbation theory that the contributions of the higher-than-the-second-order terms will be smaller than the first nonvanishing second-order term. This assumption is valid for certain systems such as the one considered in this example, however is not always the case in general as demonstrated in our previous work of VDW interaction between two odd-shaped clusters [49, 50].

2.3 Example 2: Calculation of the VDW Interaction Energy of a Pair of Identical Non-polar Atoms Using the Eigenvalue Method of Exact CDM

The eigenvalues of Eq. (34) in the general form of

$$\overset{\leftrightarrow}{\Omega} \cdot \vec{P} = u\vec{P} \tag{42}$$

can be numerically found from solving the characteristic equation of the eigenvalue problem:

$$\det\left[\overset{\leftrightarrow}{\Omega} - u\overset{\leftrightarrow}{I}\right] = 0 \tag{43}$$

After some lines of derivation, one obtains:

$$(1-u)^6 - 6\gamma^4(1-u)^4 + 9\gamma^4(1-u)^2 - 4\gamma^6 = 0 \tag{44}$$

which gives six solutions,

$$\omega_z^{\pm} = \omega_0(1 \pm 2\gamma)^{1/2}; \quad \omega_x^{\pm} = \omega_y^{\pm} = \omega_0(1 \pm \gamma)^{1/2} \tag{45}$$

Due to symmetry, the x- and y-direction normal mode frequencies are degenerate. The corresponding normal modes (eigenvectors) are listed in Table 2. Here, the dot and cross symbols indicate out-of-plane and into-the-plane direction, respectively.

Table 2 Eigenvalues and corresponding eigenmodes in a system of two atoms at separation r

⇨ ⇦	$\omega_z^+ = \omega_0(1+2\gamma)^{1/2}$
⇩ ⇩	$\omega_x^+ = \omega_0(1+\gamma)^{1/2}$
⊙ ⊙	$\omega_y^+ = \omega_0(1+\gamma)^{1/2}$
⇩ ⇧	$\omega_x^- = \omega_0(1-\gamma)^{1/2}$
⊙ ⊗	$\omega_y^- = \omega_0(1-\gamma)^{1/2}$
⇨ ⇨	$\omega_z^- = \omega_0(1-2\gamma)^{1/2}$

Now, the VDW interaction between two atoms can be obtained following Eq. (18) after subtracting the zero-point self-energy of two atoms when they are at infinite separation:

$$V_{vdw} = \frac{\hbar\omega_0}{2}\left[(1+2\gamma)^{1/2} + (1-2\gamma)^{1/2} + 2(1+\gamma)^{1/2} + 2(1-\gamma)^{1/2} - 3 - 3\right] \quad (46)$$

Here, the 3-dimensional harmonic oscillator of each atom has zero-point self-energy of $3\hbar\omega_0/2$. For $\gamma \equiv \alpha_0/r^3 < 1$, one can expand the square-root terms as done in Eq. (22) to obtain,

$$V_{vdw} = \frac{\hbar\omega_0}{2}\left[\left(-\frac{1}{8}\right)\left(12\gamma^2 + \cdots\right)\right] = -\frac{3}{4}\hbar\omega_0\frac{\alpha_0^2}{r^6} - \frac{45}{64}\hbar\omega_0\frac{\alpha_0^4}{r^{12}} - \cdots \quad (47)$$

The first non-zero term gives again the London's VDW representation. Each of the higher order terms with γ^n with $n > 2$ equals to the n-th order contribution to the dispersion interaction $W^{(n)}$. This power expansion of VDW interaction indeed corresponds to Eq. (33) for the simplest case of a two-atom system and demonstrates that the x_i shown in Eq. (33) is proportional to γ in the Drude atomic model.

2.4 Example 3: Calculation of VDW Interaction Energy of a Linear Chain of Four Identical Atoms Using TCDM

The eigenvalue problem is formulated following Eqs. (26) and (27):

$$\overleftrightarrow{\Omega}\cdot\vec{P} = \lambda^2\vec{P}$$

with

$$\overleftrightarrow{\Omega} = \begin{pmatrix} \overleftrightarrow{I} + \overleftrightarrow{Q} & \overleftrightarrow{M} \\ \overleftrightarrow{M}' & \overleftrightarrow{I} + \overleftrightarrow{Q}' \end{pmatrix}$$

Here, $\overleftrightarrow{Q} = \begin{pmatrix} 0 & \overleftrightarrow{M}_{12} \\ \overleftrightarrow{M}'_{12} & 0 \end{pmatrix}$, $\overleftrightarrow{Q}' = \begin{pmatrix} 0 & \overleftrightarrow{M}_{34} \\ \overleftrightarrow{M}'_{34} & 0 \end{pmatrix}$, $\overleftrightarrow{M} = \begin{pmatrix} \overleftrightarrow{M}_{13} & \overleftrightarrow{M}_{14} \\ \overleftrightarrow{M}_{23} & \overleftrightarrow{M}_{24} \end{pmatrix}$, and $\overleftrightarrow{M}' = \begin{pmatrix} \overleftrightarrow{M}'_{13} & \overleftrightarrow{M}'_{23} \\ \overleftrightarrow{M}'_{14} & \overleftrightarrow{M}'_{24} \end{pmatrix}$

with $\overleftrightarrow{M}_{ij} = \overleftrightarrow{M}'_{ij} = \begin{pmatrix} \gamma_{ij} & 0 & 0 \\ 0 & \gamma_{ij} & 0 \\ 0 & 0 & -2\gamma_{ij} \end{pmatrix}$ and $\gamma_{ij} \equiv \frac{\alpha_0}{r_{ij}^3} = \frac{\alpha_0}{z_{ij}^3}$.

The distance between two atoms i and j is noted as r_{ij}, and is equal to z_{ij} when the linear chain lies along z-axis as shown in Fig. 4. Now, the n-th order contribution to the dispersion interaction in the chain system becomes:

$$W^{(n)} = c_n Tr \left\{ \begin{pmatrix} \overleftrightarrow{Q} & \overleftrightarrow{M} \\ \overleftrightarrow{M}' & \overleftrightarrow{Q}' \end{pmatrix}^n \right\} \tag{48}$$

Since both $\overleftrightarrow{Q}$ and $\overleftrightarrow{Q}'$ are traceless 6 × 6 matrices,

$$\begin{aligned} Tr\, \overleftrightarrow{Q}^n &= 2\,(2 + 2^n)\gamma_{12}^n && \text{for even n } (n \geq 2) \\ Tr\, \overleftrightarrow{Q}^n &= 0 && \text{for odd n } (n \geq 1) \end{aligned}$$

And similarly,

$$\begin{aligned} Tr \left\{ \overleftrightarrow{Q}'^n \right\} &= 2\,(2 + 2^n)\gamma_{34}^n && \text{for even n } (n \geq 2) \\ Tr \left\{ \overleftrightarrow{Q}'^n \right\} &= 0 && \text{for odd n } (n \geq 1) \end{aligned}$$

On the other hand, since $\overleftrightarrow{M}_{ij}$ is a 3 × 3 diagonal matrix,

$$Tr \left\{ \overleftrightarrow{M}_{ij}^n \right\} = \left(2 + (-2)^n\right) \gamma_{ij}^n \quad \text{for all n},$$

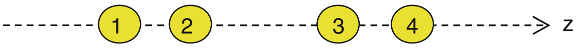


Fig. 4 A linear chain of four identical atoms

which can be delineated as:

$$\begin{aligned} &Tr\left\{\overleftrightarrow{M}_{ij}\right\} = 0 \quad \text{for n} = 1 \\ &Tr\left\{\overleftrightarrow{M}_{ij}^{n}\right\} > 0 \quad \text{for even n} \\ &Tr\left\{\overleftrightarrow{M}_{ij}^{n}\right\} < 0 \quad \text{for odd n } (> 1) \end{aligned}$$

Again, as stated earlier, both $W^{(0)}$ and $W^{(1)}$ are zero due to the cancellation of self-energies of each atom and the tracelessness of the Q and Q′ matrices, respectively.

When n = 2, $c_2 = -1/8$, and

$$\begin{aligned} Tr\left[\begin{pmatrix} \overleftrightarrow{Q} & \overleftrightarrow{M} \\ \overleftrightarrow{M}' & \overleftrightarrow{Q}' \end{pmatrix}^2\right] &= Tr\begin{pmatrix} \overleftrightarrow{Q}\overleftrightarrow{Q} + \overleftrightarrow{M}\overleftrightarrow{M}' & \overleftrightarrow{Q}\overleftrightarrow{M} + \overleftrightarrow{M}\overleftrightarrow{Q}' \\ \overleftrightarrow{M}'\overleftrightarrow{Q} + \overleftrightarrow{Q}'\overleftrightarrow{M}' & \overleftrightarrow{M}'\overleftrightarrow{M} + \overleftrightarrow{Q}'\overleftrightarrow{Q}' \end{pmatrix} \\ &= Tr\left[\overleftrightarrow{Q}\overleftrightarrow{Q} + \overleftrightarrow{M}\overleftrightarrow{M}' + \overleftrightarrow{M}'\overleftrightarrow{M} + \overleftrightarrow{Q}'\overleftrightarrow{Q}'\right] \end{aligned} \tag{49}$$

Here, $Tr\,\overleftrightarrow{Q}^2 = 12\gamma_{12}^2$, $Tr\,\overleftrightarrow{Q}'^2 = 12\gamma_{34}^2$, and $Tr\left\{\overleftrightarrow{M}\overleftrightarrow{M}'\right\} = Tr\left\{\overleftrightarrow{M}'\overleftrightarrow{M}\right\} = 6\left(\gamma_{13}^2 + \gamma_{23}^2 + \gamma_{14}^2 + \gamma_{24}^2\right)$.

Therefore, one obtains the VDW energy of a chain of four identical atoms at arbitrary separations:

$$W_{chain}^{(2)} = c_2 Tr\left[\begin{pmatrix} \overleftrightarrow{Q} & \overleftrightarrow{M} \\ \overleftrightarrow{M}' & \overleftrightarrow{Q}' \end{pmatrix}^2\right] = -\frac{3}{2}\left(\gamma_{12}^2 + \gamma_{34}^2 + \gamma_{13}^2 + \gamma_{23}^2 + \gamma_{14}^2 + \gamma_{24}^2\right) \tag{50}$$

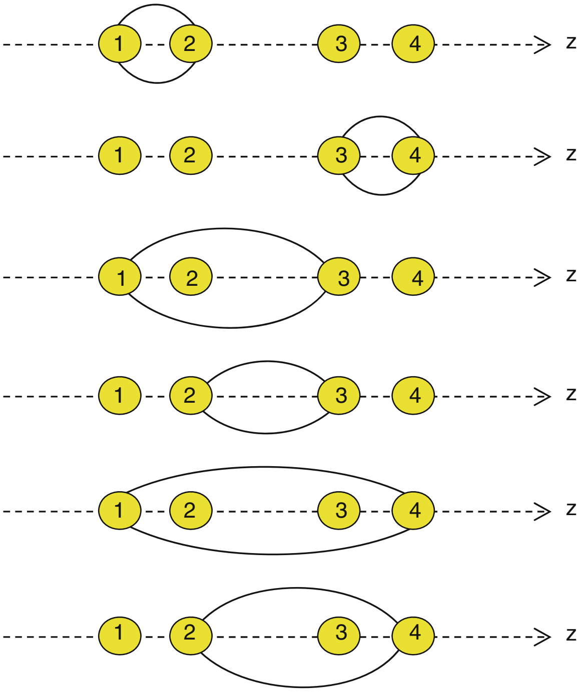
Note that this second-order contribution is a simple sum of London's pair interaction terms over all possible distinct pairs of atoms in the system. This VDW result corresponds to the VDW interaction calculated under the 2-body pair-sum approximation described in the introduction of the present chapter. Six distinct pairs listed in Eq. (50) are schematically drawn in the Fig. 5.

In the next higher-order term with n = 3, $c_3 = 1/16$ and

$$Tr\left[\begin{pmatrix} \overleftrightarrow{Q} & \overleftrightarrow{M} \\ \overleftrightarrow{M}' & \overleftrightarrow{Q}' \end{pmatrix}^3\right] = Tr\left[\overleftrightarrow{Q}^3 + \overleftrightarrow{Q}'^3 + \overleftrightarrow{M}\overleftrightarrow{M}'\overleftrightarrow{Q} + \overleftrightarrow{Q}\overleftrightarrow{M}\overleftrightarrow{M}' + \overleftrightarrow{M}'\overleftrightarrow{Q}\overleftrightarrow{M} + \overleftrightarrow{Q}'\overleftrightarrow{M}'\overleftrightarrow{M} + \overleftrightarrow{M}'\overleftrightarrow{M}\overleftrightarrow{Q}' + \overleftrightarrow{M}\overleftrightarrow{Q}'\overleftrightarrow{M}'\right]. \tag{51}$$

Here, $Tr\,\overleftrightarrow{Q}^3 = Tr\,\overleftrightarrow{Q}'^3 = 0$. Also, $Tr\left\{\overleftrightarrow{M}\overleftrightarrow{M}'\overleftrightarrow{Q}\right\} = Tr\left\{\overleftrightarrow{M}'\overleftrightarrow{Q}\overleftrightarrow{M}\right\} = Tr\left\{\overleftrightarrow{Q}\overleftrightarrow{M}\overleftrightarrow{M}'\right\}$ and $Tr\left\{\overleftrightarrow{Q}'\overleftrightarrow{M}'\overleftrightarrow{M}\right\} = Tr\left\{\overleftrightarrow{M}'\overleftrightarrow{M}\overleftrightarrow{Q}'\right\} = Tr\left\{\overleftrightarrow{M}\overleftrightarrow{Q}'\overleftrightarrow{M}'\right\}$ due to the cyclic invariance of the trace of the multiples of matrices [66]. After some calculations, one obtains

Fig. 5 Schematic diagrams of the 2nd-order many-body interaction contributions listed in Eq. (50), W$^{(2)}$



$$Tr\left\{\overset{\leftrightarrow}{M}\overset{\leftrightarrow}{M}'\overset{\leftrightarrow}{Q}\right\} = -12(\gamma_{13}\gamma_{32}\gamma_{21} + \gamma_{14}\gamma_{42}\gamma_{21})$$

and

$$Tr\left\{\overset{\leftrightarrow}{Q}'\overset{\leftrightarrow}{M}'\overset{\leftrightarrow}{M}\right\} = -12(\gamma_{34}\gamma_{41}\gamma_{13} + \gamma_{34}\gamma_{42}\gamma_{23}).$$

Therefore, the third-order contribution becomes

$$\begin{aligned} W^{(3)}_{chain} &= c_3 Tr\left[\begin{pmatrix} \overset{\leftrightarrow}{Q} & \overset{\leftrightarrow}{M} \\ \overset{\leftrightarrow}{M}' & \overset{\leftrightarrow}{Q}' \end{pmatrix}^3\right] \\ &= -\frac{9}{4}(\gamma_{13}\gamma_{32}\gamma_{21} + \gamma_{14}\gamma_{42}\gamma_{21} + \gamma_{34}\gamma_{41}\gamma_{13} + \gamma_{34}\gamma_{42}\gamma_{23}) \end{aligned} \quad (52)$$

Note here that this third-order contribution of the VDW interaction of this system corresponds to the sum of Axilrod-Teller-Muto (ATM) 3-body VDW interaction terms [18–20] for all possible distinct set of three atoms. The ATM 3-body term of one set of trio (A, B, C) then gives:

$$\Delta V_{vdw}^{ATM} = \frac{9}{8}\alpha_0^3 \frac{(1 + 3\cos\theta_A \cos\theta_B \cos\theta_C)}{r_{AB}^3\, r_{BC}^3\, r_{CA}^3}\left(\frac{1}{2}\hbar\omega_0\right) = -\frac{9}{4}\frac{\alpha_0^3}{r_{AB}^3\, r_{BC}^3\, r_{CA}^3}\left(\frac{1}{2}\hbar\omega_0\right) \tag{53}$$

Here, the angles θ_A, θ_B and θ_C are the inner angles in the triangle formed by three atoms A, B, and C, as shown in Fig. 6. In the linear configuration of the present example, since all the atoms lie in a line, two of these angles will be zero and one angle will be 180°, for example $\theta_A = \theta_B = 0$ and $\theta_C = 180°$, making the term $(1 + 3\cos\theta_A \cos\theta_B \cos\theta_C) = -2$ for any combination of three atoms A, B and C. That allows us to take the last step in the above equation.

In the system of a linear chain of four atoms, there are four sets of trio made of distinct three atoms ({1, 2, 3}, {1, 2, 4}, {3, 4, 1}, and {3, 4, 2}) as listed in Eq. (52) of $W_{chain}^{(3)}$, which are schematically drawn in Fig. 7.

When n = 4, $c_4 = -5/128$, and

$$Tr\left[\begin{pmatrix} \overleftrightarrow{Q} & \overleftrightarrow{M} \\ \overleftrightarrow{M}' & \overleftrightarrow{Q}' \end{pmatrix}^4\right] = Tr\left[\begin{array}{r} \overleftrightarrow{Q}^4 + \overleftrightarrow{Q}'^4 + \overleftrightarrow{Q}\overleftrightarrow{Q}\overleftrightarrow{M}\overleftrightarrow{M}' + \overleftrightarrow{Q}\overleftrightarrow{M}\overleftrightarrow{M}'\overleftrightarrow{Q} + \overleftrightarrow{M}\overleftrightarrow{M}'\overleftrightarrow{Q}\overleftrightarrow{Q} + \overleftrightarrow{M}'\overleftrightarrow{Q}\overleftrightarrow{Q}\overleftrightarrow{M} \\ +\overleftrightarrow{Q}'\overleftrightarrow{Q}'\overleftrightarrow{M}'\overleftrightarrow{M} + \overleftrightarrow{Q}'\overleftrightarrow{M}'\overleftrightarrow{M}\overleftrightarrow{Q}' + \overleftrightarrow{M}'\overleftrightarrow{M}\overleftrightarrow{Q}'\overleftrightarrow{Q}' + \overleftrightarrow{M}\overleftrightarrow{Q}'\overleftrightarrow{Q}'\overleftrightarrow{M}' \\ +\overleftrightarrow{Q}\overleftrightarrow{M}\overleftrightarrow{Q}'\overleftrightarrow{M}' + \overleftrightarrow{M}\overleftrightarrow{Q}'\overleftrightarrow{M}'\overleftrightarrow{Q} + \overleftrightarrow{Q}'\overleftrightarrow{M}'\overleftrightarrow{Q}\overleftrightarrow{M} + \overleftrightarrow{M}'\overleftrightarrow{Q}\overleftrightarrow{M}\overleftrightarrow{Q}' \\ +\overleftrightarrow{M}\overleftrightarrow{M}'\overleftrightarrow{M}\overleftrightarrow{M}' + \overleftrightarrow{M}'\overleftrightarrow{M}\overleftrightarrow{M}'\overleftrightarrow{M} \end{array}\right]$$

Here, $Tr\,\overleftrightarrow{Q}^4 = 36\gamma_{12}^4$, $Tr\,\overleftrightarrow{Q}'^4 = 36\gamma_{34}^4$, and $Tr\left(\overleftrightarrow{M}_{ij}\right)^4 = 18\gamma_{ij}^4$. Also,

$Tr\left[\overleftrightarrow{Q}\overleftrightarrow{Q}\overleftrightarrow{M}\overleftrightarrow{M}'\right] = Tr\left[\overleftrightarrow{Q}\overleftrightarrow{M}\overleftrightarrow{M}'\overleftrightarrow{Q}\right] = Tr\left[\overleftrightarrow{M}\overleftrightarrow{M}'\overleftrightarrow{Q}\overleftrightarrow{Q}\right] = Tr\left[\overleftrightarrow{M}'\overleftrightarrow{Q}\overleftrightarrow{Q}\overleftrightarrow{M}\right]$,
$Tr\left[\overleftrightarrow{Q}'\overleftrightarrow{Q}'\overleftrightarrow{M}'\overleftrightarrow{M}\right] = Tr\left[\overleftrightarrow{Q}'\overleftrightarrow{M}'\overleftrightarrow{M}\overleftrightarrow{Q}'\right] = Tr\left[\overleftrightarrow{M}'\overleftrightarrow{M}\overleftrightarrow{Q}'\overleftrightarrow{Q}'\right] = Tr\left[\overleftrightarrow{M}\overleftrightarrow{Q}'\overleftrightarrow{Q}'\overleftrightarrow{M}'\right]$,
$Tr\left[\overleftrightarrow{Q}\overleftrightarrow{M}\overleftrightarrow{Q}'\overleftrightarrow{M}'\right] = Tr\left[\overleftrightarrow{M}\overleftrightarrow{Q}'\overleftrightarrow{M}'\overleftrightarrow{Q}\right] = Tr\left[\overleftrightarrow{Q}'\overleftrightarrow{M}'\overleftrightarrow{Q}\overleftrightarrow{M}\right] = Tr\left[\overleftrightarrow{M}'\overleftrightarrow{Q}\overleftrightarrow{M}\overleftrightarrow{Q}'\right]$, and
$Tr\left[\overleftrightarrow{M}\overleftrightarrow{M}'\overleftrightarrow{M}\overleftrightarrow{M}'\right] = Tr\left[\overleftrightarrow{M}'\overleftrightarrow{M}\overleftrightarrow{M}'\overleftrightarrow{M}\right]$ due to cyclic invariance of the trace of multiples

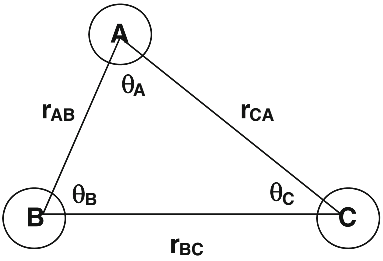


Fig. 6 The triangle in the Axilrod-Teller-Muto triple-dipole interaction

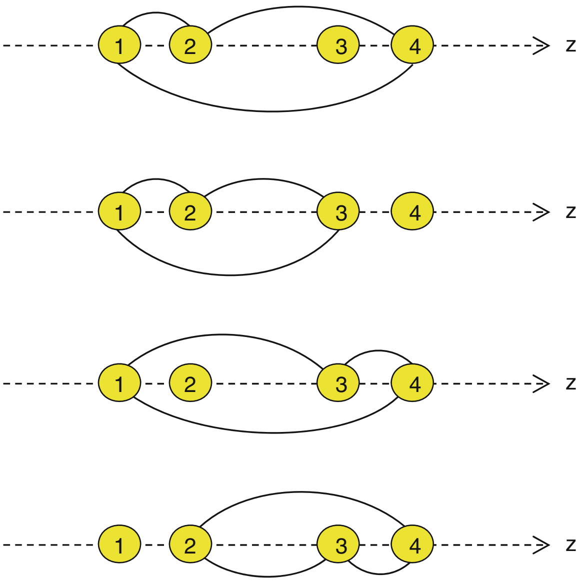


Fig. 7 Schematic diagrams of the 3rd-order many-body interaction contributions listed in Eq. (52), $W^{(3)}$

of matrices. These four distinct traces are obtained after some calculations as follows.

$$\begin{aligned} Tr\left[\overleftrightarrow{Q}\overleftrightarrow{Q}\overleftrightarrow{M}\overleftrightarrow{M}'\right] &= Tr\left[M_{12}M'_{21}M_{13}M'_{31} + M_{12}M'_{21}M_{14}M'_{41} + M_{12}M'_{21}M_{23}M'_{32} + M_{12}M'_{21}M_{24}M'_{42}\right] \\ &= 18\left(\gamma_{21}^2\gamma_{13}^2 + \gamma_{21}^2\gamma_{14}^2 + \gamma_{12}^2\gamma_{23}^2 + \gamma_{12}^2\gamma_{24}^2\right) \end{aligned}$$

$$\begin{aligned} Tr\left[\overleftrightarrow{Q}'\overleftrightarrow{Q}'\overleftrightarrow{M}'\overleftrightarrow{M}\right] &= Tr\left[M_{34}M'_{43}M'_{13}M_{31} + M'_{34}M_{43}M'_{14}M_{41} + M_{34}M'_{43}M'_{23}M_{32} + M'_{34}M_{43}M'_{24}M_{42}\right] \\ &= 18\left(\gamma_{43}^2\gamma_{31}^2 + \gamma_{34}^2\gamma_{41}^2 + \gamma_{43}^2\gamma_{32}^2 + \gamma_{34}^2\gamma_{42}^2\right) \end{aligned}$$

$$\begin{aligned} Tr\left[\overleftrightarrow{Q}\overleftrightarrow{M}\overleftrightarrow{Q}'\overleftrightarrow{M}'\right] &= 2\ Tr\left[M_{12}M_{23}M_{34}M'_{41} + M_{12}M_{24}M'_{43}M'_{31}\right] \\ &= 36\left(\gamma_{12}\gamma_{23}\gamma_{34}\gamma_{41} + \gamma_{12}\gamma_{24}\gamma_{43}\gamma_{31}\right) \end{aligned}$$

$$\begin{aligned} Tr\left[\overleftrightarrow{M}\overleftrightarrow{M}'\overleftrightarrow{M}\overleftrightarrow{M}'\right] &= Tr\begin{bmatrix} M_{13}^4 + M_{14}^4 + M_{23}^4 + M_{24}^4 \\ +2M_{31}^2M_{14}^2 + 2M_{13}^2M_{32}^2 + 2M_{14}^2M_{42}^2 + 2M_{32}^2M_{24}^2 + 4M_{13}M_{32}M_{24}M_{41} \end{bmatrix} \\ &= 18\left(\gamma_{13}^4 + \gamma_{14}^4 + \gamma_{23}^4 + \gamma_{24}^4 + 2\gamma_{31}^2\gamma_{14}^2 + 2\gamma_{13}^2\gamma_{32}^2 + 2\gamma_{14}^2\gamma_{42}^2 + 2\gamma_{32}^2\gamma_{24}^2 + 4\gamma_{13}\gamma_{32}\gamma_{24}\gamma_{41}\right) \end{aligned}$$

Thereby, the fourth-order contribution of the many-body VDW interaction becomes:

$$W_{chain}^{(4)} = -\frac{45}{32}\left[\begin{array}{l}\{\gamma_{12}^4 + \gamma_{13}^4 + \gamma_{14}^4 + \gamma_{23}^4 + \gamma_{24}^4 + \gamma_{34}^4\} \\ +2\{\gamma_{21}^2\gamma_{13}^2 + \gamma_{21}^2\gamma_{14}^2 + \gamma_{12}^2\gamma_{23}^2 + \gamma_{12}^2\gamma_{24}^2 + \gamma_{43}^2\gamma_{31}^2 + \gamma_{34}^2\gamma_{41}^2 \\ \qquad +\gamma_{43}^2\gamma_{32}^2 + \gamma_{34}^2\gamma_{42}^2 + \gamma_{31}^2\gamma_{14}^2 + \gamma_{13}^2\gamma_{32}^2 + \gamma_{14}^2\gamma_{42}^2 + \gamma_{32}^2\gamma_{24}^2\} \\ +4\{\gamma_{12}\gamma_{23}\gamma_{34}\gamma_{41} + \gamma_{12}\gamma_{24}\gamma_{43}\gamma_{31} + \gamma_{13}\gamma_{32}\gamma_{24}\gamma_{41}\}\end{array}\right] \tag{54}$$

Note here that this fourth-order contribution of the VDW interaction agrees with its general from of Eq. (1) in Ref. [36] which is derived from the fourth-order perturbation theory. Each term in the fourth-order many-body interaction contributions corresponds to distinct set of two atoms, three-atoms, and four atoms in this four-atom system. The combinations of atoms involved in Eq. (54) are schematically drawn in Fig. 8 in the order each term appears in the equation.

2.5 Example 4: Calculation of the VDW Interaction Energy of Two Dimers Lying Along the Connecting Line Using TCDM

To demonstrate the application of TCDM for the calculation of VDW interaction energy between two or more clusters of atoms, we will look at the system of four identical atoms located along a line from a different perspective. Let us consider this system of four atoms as two dimers lying along the connecting line (Fig. 9). A practical example of this system would be the linear alignment of hydrogen molecules (H_2) studied in Ref. [20]. Now, the VDW interaction energy between the two dimers can be obtained by subtracting the self-energy of each dimer from the total energy of the system. Recall that the self-energy of each dimer has already been obtained in Examples 1 and 2.

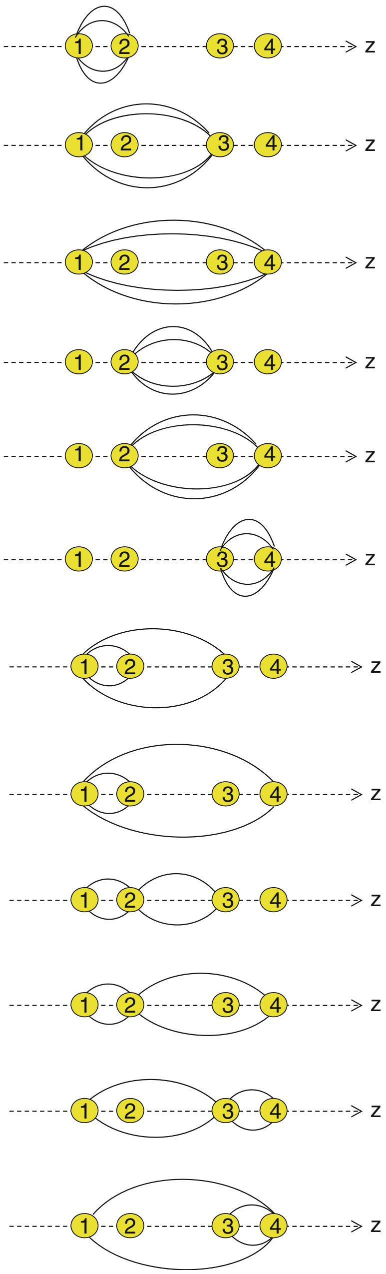
The eigenvalue problem of this system will be of the same form as derived in Example 3 for the system of a liner chain of four atoms. To estimate the VDW interaction between two dimer, however, the Eq. (48) should be modified, since now the self-energy of each dimer should be subtracted from the total energy following the general expression given in Eq. (32):

Thereby, the first nonvanishing term is the second-order many-body contribution:

$$\begin{aligned} W_{\substack{\text{two} \\ \text{dim}\,\text{er}s}}^{(2)} &= c_2 Tr\left\{\left(\overset{\leftrightarrow}{Q} \quad \begin{matrix}\overset{\leftrightarrow}{M} \\ \overset{\leftrightarrow}{M}'\end{matrix} \quad \overset{\leftrightarrow}{Q}'\right)^2\right\} - c_2 Tr\left\{\overset{\leftrightarrow}{Q}^2\right\} - c_2 Tr\left\{\overset{\leftrightarrow}{Q}'^2\right\} \\ &= -\frac{3}{2}\left(\gamma_{13}^2 + \gamma_{23}^2 + \gamma_{14}^2 + \gamma_{24}^2\right) \end{aligned} \tag{55}$$

Note that this second-order contribution is a simple sum of London's pair interactions over all possible pairs of atoms, with one atom from the first dimer (A)

Fig. 8 Schematic diagrams of the 4th-order many-body interaction contributions listed in Eq. (54), $W^{(4)}$



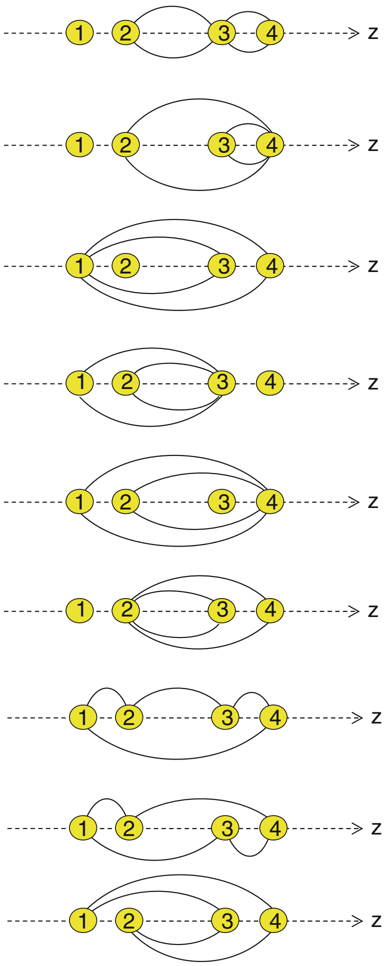


Fig. 8 continued

Fig. 9 Two identical dimers lying along the z-axis

and another from the second dimer (B), in the system. This again corresponds to the VDW interaction from calculations based on pair-sum approximation. Note that the two-body interaction terms involving two atoms that belong to the same cluster (γ_{12}^2 and γ_{34}^2 terms, in this example) are subtracted as self-energies of each cluster (or dimer, in this example).

It should be noted here that the third-order contribution of the VDW interaction between two dimers remains the same as that in the chain of four atoms which was considered in Example 3. This is because of the fact that $Tr\,\overset{\leftrightarrow}{Q}^3 = Tr\,\overset{\leftrightarrow}{Q}'^3 = 0$. Therefore, $W^{(3)}_{\substack{two\\ \text{dim ers}}} = W^{(3)}_{chain}$. In fact, $Tr\,\overset{\leftrightarrow}{Q}^n = Tr\,\overset{\leftrightarrow}{Q}'^n = 0$ for all odd n due to the tracelessness of Q and Q′ matrices. Therefore, the n-th order contribution of the VDW between two dimers or of a chain of four atoms remains the same, $W^{(n)}_{\substack{two\\ \text{dim ers}}} = W^{(n)}_{chain}$, for odd n.

3 Discussion and Concluding Remarks

The aim of this chapter is to present an overview of the CDM method which is intrinsically atomistic method which includes all the many-body interaction terms self-consistently. This rare combination of characteristics makes CDM an ideal method to calculate the VDW interaction energy involved in nanoscale systems. However, to obtain the VDW interaction energy using the eigenvalue method of exact CDM, one first needs to obtain all the eigenvalues in the eigenvalue problem of matrix size (3N × 3N) for a system composed of N particles. Usually the eigenvalue problems are solved by direct diagonalization or iterative methods. As a result, there was a concern for solving the eigenvalue problems of exact CDM for systems composed of many atoms and molecules such as those found in computer simulation studies. The computational burden is from both in memory size and in run time. As N increases, the memory size and the run time increases as N^2 and N^3, respectively. The problem with memory size can be resolved by parallelization. The burden from the run time still remains. Thereby, a memory-efficient and cost-effective computational method, TCDM, is presented.

TCDM, an alternative way to execute CDM, is to obtain VDW interaction energy by calculating the trace of the square-root of the 3N × 3N square matrix, rather than its eigenvalules. It is demonstrated in this chapter that the power series expansion in TCDM is indeed equivalent to that of the perturbation theory. Therefore, one will have to terminate the series and determine how many higher-order terms to include, unlike the eigenvalue method of exact CDM discussed above which intrinsically includes all the many-body terms. It is however shown, in our previous studies [49], that including terms less than 10 ($n < 10$) gives an excellent convergence (much less than 1 %) to the exact value of VDW Interaction energy for various configurations as listed also in Fig. 1 and Table 1 in this chapter.

A question might be raised. If TCDM is based on the power series expansion that is equivalent to that of the traditional perturbation theory, why do we use TCDM? From the perturbation theory, in principle, one can derive all the higher-order many-body interaction terms. However, most researchers have studied and/or included the contribution of three-body interactions in addition to the pair-wise sum approximation as the only many-body correction term. There has been no quantitative estimation of many-body interaction terms beyond the three-body term done using the expression derived from the perturbation theory, to the best knowledge of the author. I believe that this is because the analytic formula of the n-th order many-body term that can be derived from the perturbation theory becomes impractically cumbersome as the order n increases beyond three. Only the two-body (London formula) and three-body (ATM formula) terms have been adopted by researchers. On the other hand, in TCDM, one just needs to set up the initial 3N × 3N matrix of the eigenvalue problem of the system. The matrix multiplications are executed in the computer code which would be much more cost-effective than diagonalization. One does not need to explicitly derive the analytic form of each n-th order term. This feature of TCDM will make it practical for any interested future users to include increasingly many higher-order n-body terms as desired.

It should be noted that, although, in this chapter, two simple systems (composed of two and four identical atoms, respectively, aligned in a line) are considered as examples to explicitly demonstrate the actual execution of CDM and TCDM, the use of both methods can be extended for accurate estimates of the VDW energy in any nanoscale systems composed of dielectric materials. The formulation of exact CDM and efficient TCDM can readily be generalized for systems composed of non-identical atoms.

Finally, I would like to conclude this chapter with the following list of a few unresolved issues that can further improve our understanding of the VDW interaction:

(1) Retardation should be included as a function of inter-atomic and/or inter-cluster separation. The CDM presented in this chapter calculates the non-retarded VDW interaction. As the separation increases, larger than about 10 nm, the retardation effect gradually increases due to the finite speed of light. Even though this retardation effect is receiving increasing attention due to rapid advances in the nanotechnology in both fundamental/applied sciences and engineering, calculations have been limited to either non-retarded VDW or fully-retarded VDW interactions. One may refer chapter 6 of ref. [2], for example, for a detailed discussion of both relativistic and semi-classical methods to calculate the retarded dispersion forces at intermediate separations, but the extension of these methods to many-body systems is not a trivial problem.

(2) The higher-order multipole dispersion interaction terms beyond the dipole approximation should be investigated. Just like the higher-order many-body interaction terms, the higher-order multipole dispersion interaction terms have been commonly assumed as negligible compared to the dipole interaction terms. As the common assumption on the higher-order many-body interaction terms being small is shown incorrect for some odd-shaped nanoparticle systems [49], it is critical to test this assumption of the small higher-order multipole interaction terms in nanoscale systems.

(3) The validity of using the Clausius-Mossotti (CM) relation (see Eq. 8) in nanoscale materials should be investigated as mentioned in Sect. 2. The “effective” atomic polarizability is required as an input in calculating the VDW interaction. There has been a considerable effort made in developing the effective non-local atomic polarizability tensor using a self-consistent quantum mechanical calculation using DFT [61], which includes both bonded and non-bonded many-body interaction terms. It would be interesting to see the extension of such calculation for the larger nanoscale systems of varying shape and size to test the validity of the CM relation.

Achievement of these important and challenging tasks will allow us to accurately predict the VDW forces in nanoscale systems at varying separations as well as in those of varying shape, size and composition.

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