

Interaction between Metallic Clusters and Rare Gas Atoms

Research Report

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Van der Waals interactions between single atoms and solids are discussed for the regime of large separation. A commonly employed approximation is to evaluate this interaction as a sum of two-body interactions between the adatom and the constituent atoms of the solid. The resulting potentials are here compared with known results in various geometries and it is shown that many-body effects play an important role. We further demonstrate that screening, which is a geometrical effect, cannot be included in a simple pairwise sum model.

A new linear response density functional method entirely formulated without unoccupied Kohn-Sham orbitals is introduced. The numerical methods used to calculate the density response is discussed and applications are given. One of those applications is to compute the dispersion interaction between clusters and atoms. This is used in the simple interaction model for clusters and atoms which is derived using perturbation theory. We compare our results to the literature in two cases: the Mg-He potential and the Na-He potential.

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1 Introduction

In recent years, cluster physics has become a highly active research field. Nanoscale clusters form the bridge between the microscopic world of atoms and molecules and the macroscopic world of solids. For this reason, they have turned out to be an ideal system for studying properties of small many-body systems.

A specific technique to prepare clusters in their ground-state is by embedding them into superfluid helium nanodroplets. Techniques to agglomerate atoms and small molecules in a quantum fluid matrix — specifically, in superfluid ^4He — have opened a new and versatile way to study the structural, electronic and spectroscopic properties of nanoparticles. The droplets can be viewed as ultracold nanoscopic reactors, which isolate single molecules, clusters, or even single reactive encounters at very low temperatures. Clusters of well-defined composition can be formed inside the droplets, and their examination in the millikelvin regime has already given important clues on magnetism and superconductivity on the nanometer scale.

Over the past decade, a large amount of work on helium nanodroplets has concentrated on spectroscopic properties of *single atoms and molecules* in the superfluid environment. Experimental work on *free metal clusters* has been accompanied by corresponding theoretical studies, and whole physics Journals are devoted to the subject. Work towards a quantitative theoretical understanding of clusters and molecules *within the helium environment* is, on the other hand, much more limited: The embedded cluster is usually treated as a static perturbation to the quantum liquid matrix. In addition, only very small clusters and molecules have been treated so far. One of the reasons for this imbalance might be that established simulation techniques exist for both quantum liquids and clusters alone, but further methodological developments are needed to perform accurate simulations of the combined quantum fluid/cluster system.

Considering the embedded cluster as a static entity has a number of problems: First, according to Newton's third law, the influence of the helium matrix on the cluster is equal and of opposite sign than the influence of the cluster on the helium matrix. Second, the interaction between the cluster and individual helium atoms depends on the electronic structure of the cluster which is, in turn, affected by the helium matrix. So far, these effects were not taken into account.

The goal of my visit to Milton Cole at the Pennsylvania State University was to develop robust models for the cluster-helium interaction which take the above-mentioned effects into account. We anticipate that this work will have far-reaching applications beyond cluster physics and quantum fluids: A very active and timely field is research in the study of adsorption phenomena that are important in, for example, hydrogen storage applications.

My research report is structured as follows: In Chapter 2 the importance of many-body effects in physical adsorption and the flaw in pairwise sum models are discussed and several analytic examples are given. This chapter follows two publications, Liebrecht *et al.* [1]

(in press) and Cole *et al.* [2] (to be published in the Journal of Chemical Physics). In the following chapter, Chapter 3, a new linear response time-dependent density functional method is introduced. This new method overcomes the problem of calculating a huge number of unoccupied states because it is entirely formulated in terms of occupied Kohn-Sham orbitals and will be published soon. Chapter 4 discusses our model for the cluster-atom interaction. Results for two simple examples, the Mg-He potential and the Na-He potential, is presented and compared to the literature. In the last chapter, Chapter 5, I conclude and propose some further improvements and ideas.

2 Many-body effects in physical adsorption

2.1 The concept and method of pairwise summation

Van der Waals (VDW) interactions are associated with the electromagnetic interactions between fluctuating charges in matter [3, 4]. At temperature $T = 0$, these fluctuations arise from quantum-mechanical zero-point motion. This concept became understood soon after the development of quantum-mechanics, beginning with calculations [5, 6, 7] of the interaction $V(r_{12})$ between two atoms, 1 and 2, separated by distance r_{12} , by Wang, Eigenschitz and London. The exact result for the long-range limit can be written in terms of the atomic polarizability $\alpha(i\omega)$ of the atoms at imaginary frequency $i\omega$. This monotonically decreasing function of ω can be derived through a Kramers-Kronig transform of absorption data at real frequencies. The relevant relations are

$$V(r_{12}) = -\frac{C_6}{r_{12}^6} \quad (2.1)$$

and

$$C_6 = \frac{3\hbar}{\pi} \int_0^\infty d\omega \alpha_1(i\omega) \alpha_2(i\omega). \quad (2.2)$$

This integration is over all positive frequency ω , but the dominant contributions to the integral come from energies $\hbar\omega$ less than, or of order of, the atomic ionization energies.

A similar VDW interaction can be calculated between an atom and a semi-infinite surface, bounded by a plane, which are separated by distance z :

$$U(z) = -\frac{C_3}{z^3} \quad (2.3)$$

$$C_3 = \frac{\hbar}{4\pi} \int_0^\infty d\omega \alpha_a(i\omega) g_s(i\omega) \quad (2.4)$$

$$g_s(i\omega) \equiv \frac{\epsilon_s(i\omega) - 1}{\epsilon_s(i\omega) + 1} \quad (2.5)$$

Here $\epsilon_s(i\omega)$ is the dielectric function of the solid medium, which is assumed to be isotropic, and C_3 is the relevant coefficient [8]. These various VDW interactions are variously called dispersion forces, London forces, Lifshitz forces, and/or Casimir forces. Eqs. (2.1) and (2.3) are derived by assuming that the separation is large compared to atomic sizes, but small compared to a characteristic distance (≈ 10 nm) beyond which retardation plays a role. That *non-retarded* regime will be the focus of this paper, apart from a brief discussion of one example of retarded interactions (between an atom and a diatomic molecule). The *fully retarded* regime corresponds to separations greater than several hundred nanometers.

The preceding relations (2.2) and (2.4) are easy to evaluate if one is given the input quantities $\alpha(i\omega)$ and $g(i\omega)$, values of which are derived from experiments and/or *ab initio* calculations [9, 10]. The resulting coefficients have been tabulated extensively. The question we discuss here is how to exploit these results when dealing with other geometries, *i. e.* what interaction is appropriate in such a case? Some 75 years ago, Hamaker answered this question with an *ansatz* [11] which has been widely adopted subsequently. For the case of an atom near a solid confined within a volume Ω and constant number density n_s , he applied the form of Eq. (2.1) to the given geometry, integrating the pair interaction over the volume Ω ,

$$U^{(2)}(\mathbf{r}) = - \int_{\Omega} d^3r' \frac{C_6^{(2)} n_s}{|\mathbf{r} - \mathbf{r}'|^6}, \quad (2.6)$$

where $\mathbf{r}$ is the position of the adatom. The superscript 2 denotes the fact that 2-body interactions are assumed to accurately represent the net interaction. Hamaker desired to choose an appropriate effective value for the gas atom–solid atom VDW coefficient $C_6^{(2)}$. He did so by requiring that Eq. (2.6) yield the known result, Eq. (2.3), in the case of a half-space solid with constant number density n_s . This approach is plausible insofar as it takes into account “environmental effects” of the atoms within the solid, but one must investigate whether other effects (surface curvature, screening, ...) have adverse consequences for it. In the benchmark case of a half-space bounded by a plane, the integral in Eq. (2.6) has to yield $U(z)$ of Eq. (2.3). Therefore, we get the relation

$$C_3 = \frac{n_s \pi}{6} C_6^{(2)}. \quad (2.7)$$

Here $C_6^{(2)}$ is the effective VDW coefficient of the atom–solid atom interaction used by Hamaker. This leads to a general relation for the Hamaker potential,

$$U_{\text{Hamaker}}(\mathbf{r}) = - \frac{6}{\pi} \int_{\Omega} d^3r' \frac{C_3}{|\mathbf{r} - \mathbf{r}'|^6}. \quad (2.8)$$

By construction, this relation is exact for the case of a semi-infinite solid. By extension, it is valid at distances from the nearest surface which are small compared to the smaller of the two radii of curvature of that surface. How accurate is it for atoms in other situations? This report addresses this question for several geometries for which exact results can be calculated.

In the next section, we describe a formal expansion of the Hamaker coefficient, showing that, in general, the correction to the Hamaker 2-body approach is significant. Section 2.3 presents explicit results for the accuracy of the 2-body method in the case of atoms near free electron metals in three geometries: a semi-infinite solid, a spherical particle and a spherical cavity.

2.2 The C_3 expansion

The dielectric function $\epsilon_s(i\omega)$ of the medium, considering here a material made of just one element, can be approximated by the Clausius–Mossotti relation [12, 13]

$$\frac{\epsilon_s^{(\text{CM})}(i\omega) - 1}{\epsilon_s^{(\text{CM})}(i\omega) + 2} = \frac{4\pi}{3} n_s \alpha_s(i\omega) \equiv y_s^{(\text{CM})}(i\omega). \quad (2.9)$$

	He	Ne	Ar	Kr	Xe
$\alpha(0)$ ($\text{\AA}^3$)	0.205	0.396	1.64	2.49	4.05
$\hbar\omega$ (eV)	28.0	32.0	19.2	16.8	13.1

Table 2.1: Parameters of the rare gas atoms used in the Unsöld approximation [16], Eq. (2.14) and the Clausius–Mossotti approximation [12, 13], Eq. (2.20). Values for the static polarizabilities $\alpha(0)$ and the effective energies $\hbar\omega$ are taken from [17] and [18], respectively.

Here $\epsilon_s^{(\text{CM})}(\text{i}\omega)$ is the approximated dielectric function of the medium and $\alpha_s(\text{i}\omega)$ is the dynamic polarizability of an isolated substrate–atom. The Clausius–Mossotti approximation is exact if the chemical environment does not influence the constituents. Therefore, it takes into account classical electromagnetic screening, which is a geometrical effect, but cannot describe many–body effects related to changes in electronic structure.

If we insert $\epsilon_s^{(\text{CM})}(\text{i}\omega)$ into Eq. (2.4) we get

$$C_3^{(\text{CM})} = \frac{3\hbar}{4\pi} \int_0^\infty d\omega \alpha_a(\text{i}\omega) \frac{y_s^{(\text{CM})}(\text{i}\omega)}{2 + y_s^{(\text{CM})}(\text{i}\omega)}. \quad (2.10)$$

This leads to an expansion in the parameter $y_s^{(\text{CM})}(\text{i}\omega)$, of which the first term is given by the 2–body sum, used by Hamaker, and subsequent terms are many–body corrections,

$$C_3^{(\text{CM})} = C_3^{(2)} + C_3^{(3)} + \dots \quad (2.11)$$

with

$$C_3^{(2+j)} \equiv \frac{\hbar}{2} \left(-\frac{2\pi}{3} \right)^j n_s^{j+1} \int_0^\infty d\omega \alpha_a(\text{i}\omega) \alpha_s^{j+1}(\text{i}\omega). \quad (2.12)$$

Here we used

$$g_s^{(\text{CM})}(\text{i}\omega) = \frac{3 y_s^{(\text{CM})}(\text{i}\omega)}{2 + y_s^{(\text{CM})}(\text{i}\omega)} = 2\pi n_s \alpha_s(\text{i}\omega) \sum_{n=0}^\infty \left[-\frac{2\pi}{3} n_s \alpha_s(\text{i}\omega) \right]^n. \quad (2.13)$$

Indeed, the first correction term $C_3^{(3)}$ arises from the sum of triple dipole interactions of the form described by Axilrod, Teller and Muto [14, 15], for which the proportionality coefficient is the frequency integral in Eq. (2.12). The three atoms involved in the interaction are the external atom and two substrate atoms. The ratio of the two leading terms is of order $y_s^{(\text{CM})}(0)$, the value of which depends on the material. Note that the sign of the $C_3^{(3)}$ term is negative, while that of $C_3^{(2)}$ is positive. This difference reflects the fact that the many body contribution to C_3 is repulsive, corresponding to a screening of the 2–body interaction, *i. e.*, a reduction in the magnitude of the VDW energy, as follows mathematically from Eq. (2.13), since $g_s^{(\text{CM})}(\text{i}\omega) < \frac{3}{2} y_s^{(\text{CM})}(\text{i}\omega)$, the quantity entering the 2–body Hamaker approach. Those many–body effects become negligible in the limit of small substrate polarizability density, $\frac{2\pi}{3} n_s \alpha_s(0) \ll 1$.

Let us consider for specificity a commonly used approximation, involving 2–parameter fits to the polarizabilities of atoms and the dielectric responses of solid media, expressed in terms of characteristic frequencies and static values [16]:

$$\alpha_a(\text{i}\omega) = \frac{\alpha_a(0)}{1 + \frac{\omega^2}{\omega_a^2}} \quad (2.14)$$

	C	Cu	Ag	Mg	Li	Na	K	Rb
$\alpha(0)$ ($\text{\AA}^3$)	1.76	6.11	7.21	10.6	24.3	24.1	43.4	47.3
$\hbar\omega$ (eV)	10.8	6.10	6.28	4.54	1.91	2.22	1.85	1.91
n_s ($\text{m\AA}^{-3}$)	113	84.6	58.5	42.8	46.9	26.5	14.0	11.5

Table 2.2: Parameters of the substrate atoms used in the Unsöld approximation [16], Eq. (2.14). Values for the static polarizabilities $\alpha(0)$ are taken from Ref. [17] and all values for the atomic substrate density n_s , except graphite, can be found in the book of Ashcroft and Mermin [19]; for graphite we use Ref. [20]. The values of the effective energies $\hbar\omega$ were estimated as described in the text.

		He	Ne	Ar	Kr	Xe
graphite	C_6 ($\text{eV} \cdot \text{\AA}^6$)	4.21	8.42	29.9	43.1	63.2
	$C_3^{(\text{MB})}$ ($\text{meV} \cdot \text{\AA}^3$)	178 [8]	348 [8]	1230 [8]	1710 [8]	2470 [8]
Cu	C_6 ($\text{eV} \cdot \text{\AA}^6$)	9.71 [21]	19.7 [21]	68.4 [21]	98.8 [21]	150 [21]
	$C_3^{(\text{MB})}$ ($\text{meV} \cdot \text{\AA}^3$)	222 [8]	450 [8]	1510 [8]	2140 [8]	3050 [8]
Ag	C_6 ($\text{eV} \cdot \text{\AA}^6$)	11.8 [21]	23.9 [21]	82.4 [21]	119 [21]	179 [21]
	$C_3^{(\text{MB})}$ ($\text{meV} \cdot \text{\AA}^3$)	246 [8]	500 [8]	1640 [8]	2300 [8]	3240 [8]
Mg	C_6 ($\text{eV} \cdot \text{\AA}^6$)	12.8 [22]	25.2 [22]	95.5 [22]	140 [22]	218 [22]
	$C_3^{(\text{MB})}$ ($\text{meV} \cdot \text{\AA}^3$)	160 [23]	316 [23]	1141 [23]	1642 [23]	2475 [23]
Li	C_6 ($\text{eV} \cdot \text{\AA}^6$)	13.5 [24]	26.2 [25]	104 [25]	155 [25]	245 [25]
	$C_3^{(\text{MB})}$ ($\text{meV} \cdot \text{\AA}^3$)	123 [23]	241 [23]	902 [23]	1312 [23]	2006 [23]
Na	C_6 ($\text{eV} \cdot \text{\AA}^6$)	15.4 [24]	30.1 [25]	118 [25]	175 [25]	275 [25]
	$C_3^{(\text{MB})}$ ($\text{meV} \cdot \text{\AA}^3$)	103 [23]	203 [23]	770 [23]	1105 [23]	1695 [23]
K	C_6 ($\text{eV} \cdot \text{\AA}^6$)	23.6 [24]	46.3 [25]	179 [25]	265 [25]	417 [25]
	$C_3^{(\text{MB})}$ ($\text{meV} \cdot \text{\AA}^3$)	90.1 [23]	178 [23]	658 [23]	956 [23]	1463 [23]
Rb	C_6 ($\text{eV} \cdot \text{\AA}^6$)	26.7 [24]	52.6 [25]	201 [25]	298 [25]	466 [25]
	$C_3^{(\text{MB})}$ ($\text{meV} \cdot \text{\AA}^3$)	88.6 [23]	175 [23]	643 [23]	933 [23]	1424 [23]

Table 2.3: Values of C_6 and $C_3^{(\text{MB})}$, the exact C_3 coefficient including all many-body effects, for all gas-substrate combinations discussed in this work and their references. The C_6 values for combinations involving carbon are obtained as discussed in the text.

	C	Cu	Ag	Mg	Li	Na	K	Rb
He	0.266	0.542	0.638	0.522	1.272	0.719	0.678	0.604
Ne	0.261	0.535	0.628	0.514	1.263	0.713	0.673	0.600
Ar	0.283	0.566	0.672	0.550	1.304	0.739	0.694	0.620
Kr	0.290	0.577	0.685	0.562	1.318	0.748	0.702	0.626
Xe	0.302	0.598	0.713	0.585	1.348	0.767	0.717	0.640

Table 2.4: Values of the ratio $-C_3^{(3)}/C_3^{(2)}$ of the first many-body correction to the 2-body result for the VDW interactions involving various gas-surface combinations. Parameter values taken from Bruch, Cole and Zaremba, Appendix E [26] and Liebrecht *et al.* [1].

$$g_s(i\omega) = \frac{g_s(0)}{1 + \frac{\omega^2}{\nu_s^2}} \quad (2.15)$$

Then, one finds these analytical results for the atom-atom and atom-surface VDW interaction coefficients:

$$C_6^{a-s} = \frac{3\hbar}{2} \alpha_1(0) \alpha_2(0) \frac{\omega_1 \omega_2}{\omega_1 + \omega_2} \quad (2.16)$$

$$C_3 = \frac{\hbar}{8} g_s(0) \alpha_a(0) \frac{\nu_s \omega_a}{\nu_s + \omega_a} \quad (2.17)$$

$$C_3^{(2)} = \frac{\hbar \pi}{4} n_s \alpha_s(0) \alpha_a(0) \frac{\omega_s \omega_a}{\omega_s + \omega_a} \quad (2.18)$$

Please note that $C_3^{(2)}$ coincides with C_3 in the limit of small substrate polarizability density, as expected. The ratio of the 3-body and 2-body contributions is

$$\frac{C_3^{(3)}}{C_3^{(2)}} = -\frac{\pi}{3} n_s \alpha_s(0) \left[1 + \frac{\omega_s}{\omega_a + \omega_s} \right]. \quad (2.19)$$

The last expression also shows that the 3-body contributions become negligible in the limit of small substrate polarizability density. Table 2.4 presents values of this ratio for a series of simple gases and various surfaces. As can be seen, the ratio is significant for most of the materials presented, indicating that many-body corrections to the 2-body sum are important, indeed.

The values used for the static polarizabilities $\alpha(0)$, the effective energies $\hbar\omega$ and the atomic substrate densities n_s together with their references are listed in Table 2.1 and Table 2.2. The values and references for C_6 and $C_3^{(\text{MB})}$ can be found in Table 2.3. These C_6 coefficients were supplemented by a recently calculated C_6 coefficient for carbon-carbon interaction [27] and combined with Eq. (2.14) to obtain $\hbar\omega$ of the substrate atoms. The van der Waals coefficients for carbon-rare gas combinations were determined with Eq. (2.14).

2.3 Qualitative results for atoms near metal surfaces

In the case of metallic surfaces, exact results have been derived for the VDW interaction for a number of simple geometries (*e.g.* atom interacting with a half-space metal, a spherical particle or inside a spherical or cylindrical cavity). The method and its results are summarized in the review of Schmeits and Lucas [28, 29], as well as the monograph of Parsegian

[3]. In such cases, we can compare these results with those obtained with the approximate Hamaker approach described above. We focus here on VDW interactions derived for three situations: an atom near a half-space metal, a spherical particle and an atom inside a spherical cavity.

2.3.1 Atom interacting with a half-space metal

Using the Clausius–Mossotti relation [12, 13], Eq. (2.9), and the Unsöld approximation [16], Eq. (2.14), we can evaluate Eq. (2.10) directly and obtain following relation between $C_3^{(\text{CM})}$ and $C_3^{(2)}$,

$$\frac{C_3^{(2)}}{C_3^{(\text{CM})}} = \frac{\omega_s}{\omega_s + \omega_a} \eta^2 + \frac{\omega_a}{\omega_s + \omega_a} \eta \quad (2.20)$$

with the screening parameter

$$\eta \equiv \sqrt{1 + \frac{2\pi}{3} n_s \alpha_s(0)}. \quad (2.21)$$

Eq. (2.20) expresses the many-body effects explicitly as a function of η and the two relevant frequencies, ω_a and ω_s . One can evaluate this general expression without specifying these individual energies in three simple limits, depending on the ratio ω_a/ω_s . Fig. 2.1 presents values of the ratio $C_3^{(2)}/C_3^{(\text{MB})}$, where $C_3^{(\text{MB})}$ represents the correct C_3 coefficient including all many-body effects, as three curves corresponding to these limits, which are specified in the caption. One observes an overall consistency between the trend of all three curves and the data for specific systems. The many-body effects are significant. Fig. 2.2 depicts the dependence of the screening-corrected ratio $C_3^{(\text{CM})}/C_3^{(\text{MB})}$ on η . The deviation of the data points from 1 is significantly reduced. The same is true for the variation among the rare gas atoms for a fixed substrate; note that the values for He and Ne are the lowest among the various gases while those for Xe are the highest. The figure shows a general trend, except for Ag, that the deviation increases with the screening parameter η . This suggests that many-body effects of the substrate become more important as the substrate becomes more polarizable and the substrate's electrons more delocalized. A linear fit of the form $k(\eta - 1) + d$ to all data points yields $k = 0.506 \pm 0.096$ and $d = 1.007 \pm 0.048$ and is shown in Fig 2.2. Please note that the value for d is consistent with the low-density limit of 1. To explain the discrepancy for Ag we refer to experimental and theoretical studies of low energy ion scattering (LEIS) of He^+ at noble metal surfaces [30, 31]: A jellium model for the substrate can describe the experimental results for Cu, whereas the same model fails for Ag. To explain the experimental results for Ag, the model has to be extended to include the $4d$ -electrons of Ag. In our work we only account for the outermost s -electrons of Cu and Ag to obtain the coefficients $C_3^{(2)}$ and $C_3^{(\text{CM})}$ and we get, in agreement with the LEIS experiments, a discrepancy for Ag.

2.3.2 Atom interacting with a spherical particle

In this case, the potential energy takes the following form, for the case of an atom at radial distance D from the center of a spherical particle of radius a :

$$V_{\text{sp}}(D) = -\frac{\hbar}{2\pi D^3} \sum_{l=1}^{\infty} (l+1)(2l+1) \left(\frac{a}{D}\right)^{2l+1} \int_0^{\infty} d\omega \alpha_a(i\omega) \frac{\epsilon_s(i\omega) - 1}{\epsilon_s(i\omega) + \frac{l+1}{l}} \quad (2.22)$$

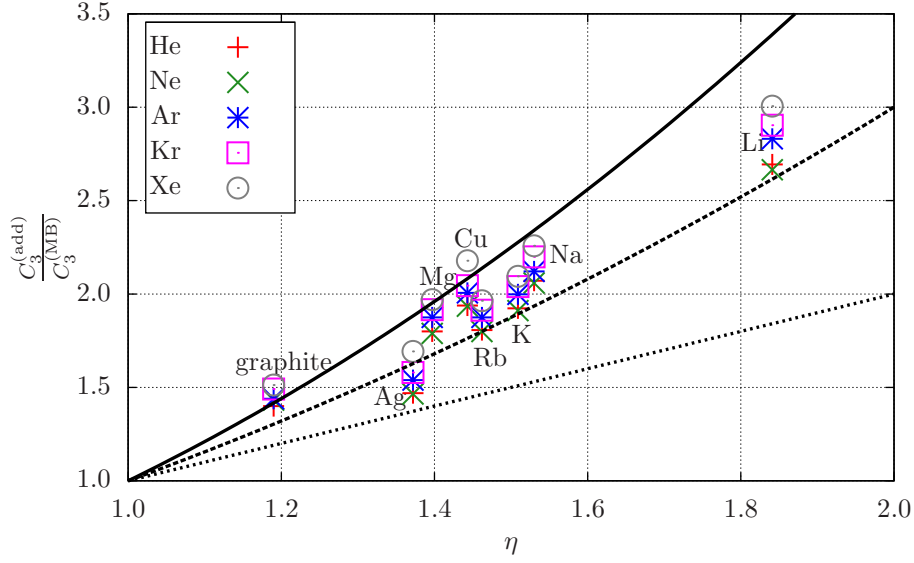


Figure 2.1: Dependence on the screening parameter η , defined in Eq. (2.21), of the ratio of the coefficient $C_3^{(\text{add})}$ computed with the additivity approximation to its many-body (correct) value $C_3^{(\text{MB})}$, for various gas-substrate combinations. The three curves show the ratio of $C_3^{(\text{add})}$ to its screening-corrected value $C_3^{(\text{CM})}$ and assume (from top to bottom) $E_g \ll E_s$, $E_g = E_s$ and $E_g \gg E_s$, respectively.

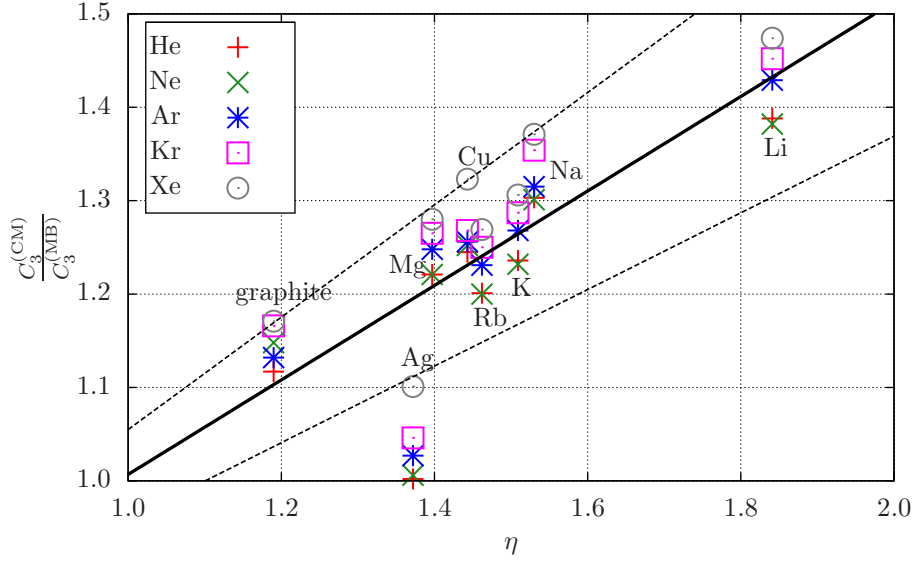


Figure 2.2: Dependence on the screening parameter η , defined in Eq. (2.21), of the ratio of the coefficient $C_3^{(\text{CM})}$ from Eq. (2.20) to its many-body (correct) value $C_3^{(\text{MB})}$, for various gas-substrate combinations. The solid curve shows a linear fit of the form $k(\eta - 1) + d$ to all data points ($k = 0.506 \pm 0.096$, $d = 1.007 \pm 0.048$). The dashed curves depict the statistical standard deviation of the fit.

This expression can be shown to yield the usual form ($-\frac{C_6}{z^6}$) in the limit of close approach, *i.e.*, $D - a \ll a$, as it must. Let us consider the opposite limit, $D \gg a$. In this limit approaching infinite separation and using the Clausius–Mossotti relation, Eq. (2.9), the leading term is $l = 1$ and the result is

$$V_{\text{sp}}^{\text{CM}}(D \rightarrow \infty) \rightarrow -\frac{3\hbar a^3}{\pi D^6} I \quad (2.23)$$

where

$$I \equiv \int_0^\infty d\omega \alpha_a(i\omega) \frac{\epsilon_s(i\omega) - 1}{\epsilon_s(i\omega) + 2} = \frac{4\pi}{3} n_s \int_0^\infty d\omega \alpha_a(i\omega) \alpha_s(i\omega) = \frac{4\pi^2}{9\hbar} n_s C_6^{a-s}. \quad (2.24)$$

The integral I is seen to be essentially that entering into the expression for the VDW coefficient C_6^{a-s} of the atom–solid atom interaction. Letting $N_s = \frac{4\pi}{3} n_s a^3$, the number of atoms in the solid particle, we arrive at the following limiting behavior:

$$V_{\text{sp}}^{\text{CM}}(D \rightarrow \infty) \rightarrow -N_s \frac{C_6^{a-s}}{D^6} \quad (2.25)$$

This is a simple, but remarkable, result. It indicates that the interaction between a spherical particle and a distant atom is equal to N_s times the interaction from a single solid atom interacting with the distant atom. In other words, there are no geometrical many–body effects. This behavior obtains because of the symmetry of the spherical particle (which cancels screening effects) and the large distance from the atom. We contrast this behavior with what would be the result in the Hamaker approach, $V_{\text{sp}}^{\text{Hamaker}}$; the ratio of interactions is

$$\frac{V_{\text{sp}}^{\text{Hamaker}}(D \rightarrow \infty)}{V_{\text{sp}}^{\text{CM}}(D \rightarrow \infty)} = \frac{C_6^{(2)}}{C_6^{a-s}} = \frac{6}{\pi n_s} \frac{C_3}{C_6^{a-s}}. \quad (2.26)$$

This ratio can be evaluated for the same sets of gas–solid combinations as appear in Table 2.4. The deviation from unity is significant. The origin of this discrepancy is that the coefficient $C_6^{(2)}$ was derived from a situation (atom near half–space) for which screening plays an important role in reducing the interaction. Hence, its value is depressed below the actual value, C_6^{a-s} ; this screening is absent from the present geometry (atom far from spherical particle), so the preceding ratio falls below one.

We note in passing that the present problem can be solved quite directly in the large D limit without exploiting the general formula, Eq. (2.22), presented above. The reason is that for $D \gg a$, the problem becomes that of a point particle (the sphere) interacting with the distant atom. In such a case, we can use the general expression ($V_{\text{sp}} \propto -\frac{C_6^{\text{a-particle}}}{D^6}$), inserting the appropriate VDW coefficient $C_6^{\text{a-particle}}$. This requires that we know the polarizability of the spherical particle of radius a , which is given by

$$\alpha_{\text{sphere}}(i\omega) = \frac{\epsilon(i\omega) - 1}{\epsilon(i\omega) + 1} a^3. \quad (2.27)$$

Inserting this relation into the general expression for C_6 and using the Clausius–Mossotti relation, Eq. (2.9), yields

$$C_{6,\text{CM}}^{\text{a-particle}} = N_s C_6^{a-s}. \quad (2.28)$$

This coincides with what was described above as the result manifesting the absence of geometric many–body effects.

To include many–body effects related to the chemical environment in the sphere, we can try a similar approach to Hamaker’s. The only difference is that we use the results obtained by the

Clausius–Mossotti approximation as the starting point, rather than the pair summation. We have seen that the Clausius–Mossotti approximation yields $C_{6,\text{CM}}^{\text{a-particle}}$, see Eq. (2.28). The correct coefficient, which also includes many–body effects due to the chemical environment, will be denoted by $C_{6,\text{MB}}^{\text{a-particle}}$. Please note that

$$\lim_{N_s \rightarrow 1} C_{6,\text{CM}}^{\text{a-particle}} = C_{6,\text{MB}}^{\text{a-particle}}. \quad (2.29)$$

Therefore, the result obtained by the Clausius–Mossotti approximation might be a good estimate for $C_{6,\text{MB}}^{\text{a-particle}}$ in the case of small N_s . In the opposite limit, it is clear that changes in the electronic structure become more and more important and lead to additional effects. In previous work [1], we studied those effects in the case of atom–surface interactions for various rare gas – substrate combinations. We had access to exact C_3 coefficients, $C_3^{(\text{MB})}$, and used the Clausius–Mossotti approximation to calculate $C_3^{(\text{CM})}$. We can use them to estimate $C_{6,\text{MB}}^{\text{a-particle}}$,

$$C_{6,\text{MB}}^{\text{a-particle}} = C_{6,\text{CM}}^{\text{a-particle}} \frac{C_{6,\text{MB}}^{\text{a-particle}}}{C_{6,\text{CM}}^{\text{a-particle}}} \approx C_{6,\text{CM}}^{\text{a-particle}} \frac{C_3^{(\text{MB})}}{C_3^{(\text{CM})}}. \quad (2.30)$$

This approximation should hold for large N_s , where the chemical environment is very bulk–like, but breaks down for small N_s , as expected. Thus, VDW interactions involving small particles behave very differently from those involving large particles.

2.3.3 Atom inside a spherical cavity

We turn now to the case of an atom inside a spherical cavity. In this case we use the general relationship [28]

$$V_{\text{cav}}(D) = -\frac{\hbar\omega_a\alpha_a(0)}{4D^3} \sum_{l=1}^{\infty} l(2l+1) \left(\frac{D}{a}\right)^{2l+1} \left[1 + \frac{\omega_a}{\omega_P} \left(\frac{2l+1}{l+1}\right)^{\frac{1}{2}}\right]^{-1}. \quad (2.31)$$

Here ω_P is the plasma frequency of the material surrounding the cavity. Let $x = \frac{\omega_a}{\omega_P}$. We focus on the value at the center of the cavity, *i.e.* the origin, $D = 0$. Then only the $l = 1$ term contributes and we find

$$V_{\text{cav}}(D \rightarrow 0) \rightarrow -\frac{3}{4} \frac{\hbar\omega_a\alpha_a(0)}{a^3 (1 + \sqrt{3/2}x)}. \quad (2.32)$$

Now the Hamaker method yields (by integrating over the solid)

$$V_{\text{cav}}^{\text{Hamaker}}(D) = -\frac{\hbar\omega_a\alpha_a(0)}{1+x} \frac{a^3}{(a^2 - D^2)^3}. \quad (2.33)$$

At the center, $D = 0$, this becomes

$$V_{\text{cav}}^{\text{Hamaker}}(D \rightarrow 0) \rightarrow -\frac{\hbar\omega_a\alpha_a(0)}{a^3 (1+x)}. \quad (2.34)$$

The ratio of approximate to exact interactions is thus given by

$$\frac{V_{\text{cav}}^{\text{Hamaker}}(D \rightarrow 0)}{V_{\text{cav}}(D \rightarrow 0)} = \frac{4}{3} \frac{1 + \sqrt{3/2}x}{1+x} \quad (2.35)$$

Thus, the Hamaker method significantly overestimates the magnitude of the VDW interaction. The ratio is 0.75 for small x and ≈ 1.63 for very large values of x . Note that the corresponding ratio was less than one for the previously considered case, an atom outside of a particle. Thus, the correction to the Hamaker approach can be to either enhance or weaken the VDW interaction, depending on the geometry. The behavior in the case of an atom inside a cylindrical pore, incidentally, is similar to the spherical pore case — the Hamaker method overestimates the interaction strength.

3 Linear response time-dependent density functional theory formulated without unoccupied orbitals

3.1 The many-body problem

At microscopic scales, for systems comprised of up to several thousand atoms, physics is to a large part governed by Schrödinger’s equation [32]. The full many-body problem for such systems is very complicated and it is unavoidable to make approximations. One of these possible approximations is well known and called Born–Oppenheimer approximation [33]. In this approximation, the motion of the “fast” electrons can be separated from the much slower motion of the nuclei because of the large ratio between their masses. This is a tremendous simplification of the original problem: The electrons now move in a static, external potential generated by the nuclei. While the electrons have to be treated quantum-mechanically, the motion of the nuclei can, in most cases, be treated classically.

The electronic many-body Schrödinger equation resulting from the Born–Oppenheimer approximation for N electrons is

$$\hat{H}\psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = [\hat{T} + \hat{U} + \hat{V}] \psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = E\psi(\mathbf{r}_1, \dots, \mathbf{r}_N). \quad (3.1)$$

The kinetic energy operator is given by

$$\hat{T} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 \quad (3.2)$$

where $\hbar$ is the reduced Planck constant and m is the electron mass. The electron–electron interaction can be written as

$$\hat{U} = \sum_{i < j} u(\mathbf{r}_i, \mathbf{r}_j) = \sum_{i < j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (3.3)$$

For a molecule or a solid, the external potential has the form

$$\hat{V} = - \sum_{i,k} \frac{z_k e^2}{|\mathbf{r}_i - \mathbf{R}_k|} \quad (3.4)$$

where $\mathbf{R}_k$ and z_k are the positions and charges of the nuclei, respectively. Note that $\hat{T}$ and $\hat{U}$ are the same for all electronic systems. Such operators are called universal operators. So the difference in the properties of electronic systems (whether it is an atom, a molecule or a solid) enters solely in the definition of the external potential $\hat{V}$.

Unfortunately, equation (3.1) is even for small systems far too complicated to solve it in a naive way. The main problem, besides long computing time, is a memory problem. If we consider a system of N interacting particles, we need $3N$ spatial and N spin coordinates to describe it. The many-body wave functions ψ then would be a function in $4N$ coordinates. To solve Schrödinger's equation on a computer we have to discretize these functions. This can be very memory-consuming. Consider, for example, the very simple molecule C_2H_6 containing 30 electrons. If we assume a storage density of one byte per cubic Bohr a_0^3 , in future storage media, we would need about one million times the volume of the universe to store one wave function alone [34].

3.2 Static density functional theory

According to the first Hohenberg–Kohn theorem [35], the total energy E_0 of an time-independent system depends only on the ground state density n_0 . It is given by

$$E_0 = E[n_0] \equiv F[n_0] + V[n_0], \quad (3.5)$$

where

$$F[n] \equiv T[n] + U[n] \quad (3.6)$$

is the sum of the kinetic energy functional $T[n]$ and the electron–electron interaction functional $U[n]$, which are general functionals of the electronic density $n(\mathbf{r})$.

$$V[n] \equiv \int d^3r v(\mathbf{r})n(\mathbf{r}) \quad (3.7)$$

is the external potential functional. The second Hohenberg–Kohn theorem [35] states that one can find the ground state density $n_0(\mathbf{r})$ by minimizing $E[n]$, $E[n_0] \leq E[n]$. These two theorems build the fundamental basis for density functional theory (DFT).

A common way to minimize the energy functional was proposed by Kohn and Sham [36]. The interacting system of electrons is described by an auxiliary system of non-interacting particles. The connection between the two systems is the electronic density $n(\mathbf{r})$, which is the same for both,

$$n(\mathbf{r}) = \sum_{\sigma} n_{\sigma}(\mathbf{r}) = \sum_{i,\sigma} f_{i,\sigma} |\varphi_{i,\sigma}(\mathbf{r})|^2. \quad (3.8)$$

Here the $n_{\sigma}(\mathbf{r})$ are spin densities and $f_{i,\sigma}$ is the occupation number of orbital $\varphi_{i,\sigma}(\mathbf{r})$ with orbital number i and spin σ . The total energy functional becomes

$$E[n_{\uparrow}, n_{\downarrow}] = T_{\text{ks}}[n_{\uparrow}, n_{\downarrow}] + U_{\text{H}}[n] + V[n] + E_{\text{xc}}[n_{\uparrow}, n_{\downarrow}] \quad (3.9)$$

where

$$T_{\text{ks}}[n_{\uparrow}, n_{\downarrow}] \equiv -\frac{\hbar^2}{2m} \sum_{i,\sigma} \int d^3r \varphi_{i,\sigma}^*(\mathbf{r}) \Delta \varphi_{i,\sigma}(\mathbf{r}) \quad (3.10)$$

is the kinetic energy of the non-interacting system,

$$U_{\text{H}}[n] \equiv \frac{e^2}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (3.11)$$

is the direct term of the electron–electron interaction and

$$E_{\text{xc}}[n_{\uparrow}, n_{\downarrow}] \equiv T[n_{\uparrow}, n_{\downarrow}] - T_{\text{ks}}[n_{\uparrow}, n_{\downarrow}] + U[n] - U_{\text{H}}[n] \quad (3.12)$$

is the so-called exchange–correlation functional. It represents the energy difference between the interacting system to the non-interacting system.

To calculate the electronic ground state density one has to minimize Eq. (3.9) with the additional constraint of particle conservation. The resulting equations are,

$$\left[-\frac{\hbar^2}{2m}\Delta + v_{\text{ks}}^{(\sigma)}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}) \right] \varphi_{i,\sigma}(\mathbf{r}) = \epsilon_{i,\sigma} \varphi_{i,\sigma}(\mathbf{r}) \quad (3.13)$$

and

$$n(\mathbf{r}) = \sum_{\sigma} n_{\sigma}(\mathbf{r}) = \sum_{i,\sigma} f_{i,\sigma} |\varphi_{i,\sigma}(\mathbf{r})|^2 \quad (3.14)$$

with the effective potential $v_{\text{ks}}^{(\sigma)}[n_{\uparrow}, n_{\downarrow}](\mathbf{r})$,

$$v_{\text{ks}}^{(\sigma)}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}) \equiv v(\mathbf{r}) + v_{\text{H}}[n](\mathbf{r}) + v_{\text{xc}}^{(\sigma)}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}). \quad (3.15)$$

This effective potential consists of the external potential $v(\mathbf{r})$, the Hartree potential

$$v_{\text{H}}[n](\mathbf{r}) \equiv e^2 \int d^3 r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (3.16)$$

and the exchange–correlation potential

$$v_{\text{xc}}^{(\sigma)}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}) \equiv \frac{\delta E_{\text{xc}}[n_{\uparrow}, n_{\downarrow}]}{\delta n_{\sigma}(\mathbf{r})}. \quad (3.17)$$

To use Dirac's notation, we introduce the operators $\hat{t}_{\text{ks}}, \hat{v}_{\text{ks}}^{(\sigma)}[n_{\uparrow}, n_{\downarrow}]$ and

$$\hat{h}_{\text{ks}}^{(\sigma)}[n_{\uparrow}, n_{\downarrow}] \equiv \hat{t}_{\text{ks}} + \hat{v}_{\text{ks}}^{(\sigma)}[n_{\uparrow}, n_{\downarrow}], \quad (3.18)$$

which are defined by their application to a arbitrary state $|\psi\rangle$ in real-space,

$$\hat{t}_{\text{ks}} |\psi\rangle \equiv \int d^3 r' t(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}') \equiv -\frac{\hbar^2}{2m} \Delta \psi(\mathbf{r}), \quad (3.19)$$

$$\hat{v}_{\text{ks}}^{(\sigma)}[n_{\uparrow}, n_{\downarrow}] |\psi\rangle \equiv \int d^3 r' v_{\text{ks}}^{(\sigma)}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \psi(\mathbf{r}') = v_{\text{ks}}^{(\sigma)}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}) \psi(\mathbf{r}) \quad (3.20)$$

and

$$\begin{aligned} \hat{h}_{\text{ks}}^{(\sigma)}[n_{\uparrow}, n_{\downarrow}] |\psi\rangle &\equiv \int d^3 r' h_{\text{ks}}^{(\sigma)}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}') \\ &\equiv \left[-\frac{\hbar^2}{2m} \Delta + v_{\text{ks}}^{(\sigma)}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}) \right] \psi(\mathbf{r}). \end{aligned} \quad (3.21)$$

The total ground state energy E_0 of the interacting system is given by

$$\begin{aligned} E_0 &= \sum_{i,\sigma} f_{i,\sigma} \epsilon_{i,\sigma} - U_{\text{H}}[n] - \int d^3 r n(\mathbf{r}) v_{\text{xc}}^{(\sigma)}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}) + E_{\text{xc}}[n_{\uparrow}, n_{\downarrow}] \\ &= \sum_{i,\sigma} f_{i,\sigma} \left\langle \varphi_{i,\sigma} \left| \hat{h}_{\text{ks}}^{(\sigma)}[n_{\uparrow}, n_{\downarrow}] \right| \varphi_{i,\sigma} \right\rangle - U_{\text{H}}[n] - \int d^3 r n(\mathbf{r}) v_{\text{xc}}^{(\sigma)}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}) + E_{\text{xc}}[n_{\uparrow}, n_{\downarrow}]. \end{aligned} \quad (3.22)$$

3.3 Time-dependent density functional theory

The time-dependent DFT is very similar to the time-independent version. The generalization of the Hohenberg–Kohn theorems [35] to time-dependent functionals is the Runge–Gross theorem [37]. The Kohn–Sham equations for the time-dependent case are

$$\left[-\frac{\hbar^2}{2m}\Delta + v_{\text{ks}}^{(\sigma)}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}; t) \right] \varphi_{i,\sigma}(\mathbf{r}; t) = i\hbar \frac{\partial}{\partial t} \varphi_{i,\sigma}(\mathbf{r}; t) \quad (3.23)$$

and

$$n(\mathbf{r}; t) = \sum_{\sigma} n_{\sigma}(\mathbf{r}; t) = \sum_{i,\sigma} f_{i,\sigma} |\varphi_{i,\sigma}(\mathbf{r}; t)|^2 \quad (3.24)$$

with the effective potential $v_{\text{ks}}^{(\sigma)}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}; t)$,

$$v_{\text{ks}}^{(\sigma)}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}; t) \equiv v(\mathbf{r}; t) + v_{\text{H}}[n](\mathbf{r}; t) + v_{\text{xc}}^{(\sigma)}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}; t). \quad (3.25)$$

The different contributions to this effective potential are defined as for the static case.

One can derive these Kohn–Sham equations using the Lagrangian density

$$\begin{aligned} \mathcal{L}(t) = & \sum_{i,\sigma} f_{i,\sigma} \left\langle \varphi_{i,\sigma} \left| \hat{h}_{\text{ks}}^{(\sigma)}[n_{\uparrow}, n_{\downarrow}](t) - i\hbar \frac{\partial}{\partial t} \right| \varphi_{i,\sigma} \right\rangle - U_{\text{H}}[n](t) \\ & - \sum_{\sigma} \int d^3r n_{\sigma}(\mathbf{r}; t) v_{\text{xc}}^{(\sigma)}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}; t) + E_{\text{xc}}[n_{\uparrow}, n_{\downarrow}](t) \end{aligned} \quad (3.26)$$

and the corresponding action integral

$$\mathcal{S} = \int_{t_1}^{t_2} dt \mathcal{L}(t). \quad (3.27)$$

The equations of motion for $\varphi_{i,\sigma}(\mathbf{r}; t)$ and $\varphi_{i,\sigma}^*(\mathbf{r}; t)$,

$$\frac{\partial \mathcal{S}}{\partial \varphi_{i,\sigma}^*(\mathbf{r}; t)} - \frac{d}{dt} \frac{\partial \mathcal{S}}{\partial \dot{\varphi}_{i,\sigma}^*(\mathbf{r}; t)} = 0 \quad \text{and} \quad \frac{\partial \mathcal{S}}{\partial \varphi_{i,\sigma}(\mathbf{r}; t)} - \frac{d}{dt} \frac{\partial \mathcal{S}}{\partial \dot{\varphi}_{i,\sigma}(\mathbf{r}; t)} = 0 \quad (3.28)$$

are equivalent to Eq. (3.23) and its complex conjugate.

3.4 Linear response

If we add a small perturbation $\delta v(\mathbf{r}; t)$ to a static Hamiltonian in Eq. (3.23), we can use the properties of the undisturbed system and try to approximate quantities in the perturbed one. This procedure is relatively simple but can lead to unphysical divergences if not handled correctly, for example in the case of a homogeneous electron gas.

The disturbed ground state density can be expressed as

$$n'(\mathbf{r}; t) = n(\mathbf{r}) + \delta n(\mathbf{r}; t) = \sum_{\sigma} n_{\sigma}(\mathbf{r}) + \sum_{\sigma} \delta n_{\sigma}(\mathbf{r}; t), \quad (3.29)$$

where $n(\mathbf{r})$ represents the density of the undisturbed system and $\delta n(\mathbf{r}; t)$ the difference between the disturbed and undisturbed system. The ground state of the undisturbed system is characterized by the orbitals $\varphi_{i,\sigma}(\mathbf{r})$ and $f_{i,\sigma}$. Since $\delta v(\mathbf{r}; t)$ is assumed to be small, we further assume that the occupation numbers of the disturbed system are identical to those of the undisturbed one, $f'_{i,\sigma} = f_{i,\sigma}$, and that the disturbed and undisturbed Kohn–Sham orbitals only differ by a small correction $\delta\varphi_{i,\sigma}(\mathbf{r}; t)$,

$$\varphi'_{i,\sigma}(\mathbf{r}; t) = \frac{e^{-i\frac{E_0}{N}\frac{t}{\hbar}}}{\mathcal{N}_{i,\sigma}(t)} \left[\varphi_{i,\sigma}(\mathbf{r}) + \delta\varphi_{i,\sigma}(\mathbf{r}; t) \right]. \quad (3.30)$$

Here $\mathcal{N}_{i,\sigma}(t)$ ensures normalization. If we linearize Eq. (3.29) we get

$$\begin{aligned} n'(\mathbf{r}; t) &= \sum_{h,\sigma} \frac{f_{h,\sigma}}{\mathcal{N}_{h,\sigma}^2(t)} |\varphi'_{h,\sigma}(\mathbf{r}; t)|^2 \\ &= n(\mathbf{r}) + \sum_{h,\sigma} f_{h,\sigma} \left[\varphi_{h,\sigma}^*(\mathbf{r}) \delta\varphi_{h,\sigma}(\mathbf{r}; t) + \varphi_{h,\sigma}(\mathbf{r}) \delta\varphi_{h,\sigma}^*(\mathbf{r}; t) \right] + \mathcal{O}(|\delta\varphi_{h,\sigma}|^2), \end{aligned} \quad (3.31)$$

which allows us to identify

$$\delta n_\sigma(\mathbf{r}; t) = \sum_h f_{h,\sigma} \left[\varphi_{h,\sigma}^*(\mathbf{r}) \delta\varphi_{h,\sigma}(\mathbf{r}; t) + \varphi_{h,\sigma}(\mathbf{r}) \delta\varphi_{h,\sigma}^*(\mathbf{r}; t) \right]. \quad (3.32)$$

In linear response theory $\delta n_\sigma(\mathbf{r}; t)$ is connected to $\delta v(\mathbf{r}; t)$ by

$$\delta n_\sigma(\mathbf{r}; t) = \int_0^\infty d\tau \int d^3r' \chi^{(\sigma)}(\mathbf{r}, \mathbf{r}'; \tau) \delta v(\mathbf{r}'; t - \tau). \quad (3.33)$$

The function $\chi_\sigma(\mathbf{r}, \mathbf{r}'; t)$ is the so-called linear spin response function of the system under consideration. Using Laplace transforms this can be written as

$$\delta \bar{n}_\sigma(\mathbf{r}; s) = \int d^3r' \bar{\chi}^{(\sigma)}(\mathbf{r}, \mathbf{r}'; s) \delta \bar{v}(\mathbf{r}'; s), \quad (3.34)$$

with

$$\delta \bar{v}(\mathbf{r}; s) = \int_0^\infty dt e^{-st} \delta v(\mathbf{r}; t), \quad (3.35)$$

$$\delta \bar{n}_\sigma(\mathbf{r}; s) = \int_0^\infty dt e^{-st} \delta n_\sigma(\mathbf{r}; t) \quad (3.36)$$

and

$$\bar{\chi}^{(\sigma)}(\mathbf{r}, \mathbf{r}'; s) = \int_0^\infty dt e^{-st} \chi^{(\sigma)}(\mathbf{r}, \mathbf{r}'; t). \quad (3.37)$$

3.4.1 Langrangian density

The Lagrangian density of the perturbed system is

$$\begin{aligned} \mathcal{L}(t) &= \sum_{i,\sigma} f_{i,\sigma} \left\langle \varphi'_{i,\sigma} \left| \hat{h}_{\text{KS}}^{(\sigma)}[n'_\uparrow, n'_\downarrow] + \delta \hat{v}(t) - i\hbar \frac{\partial}{\partial t} \right| \varphi'_{i,\sigma} \right\rangle \\ &\quad - U_{\text{H}}[n'](t) - \sum_\sigma \int d^3r n'_\sigma(\mathbf{r}; t) v_{\text{xc}}^{(\sigma)}[n'_\uparrow, n'_\downarrow](\mathbf{r}; t) + E_{\text{xc}}[n'_\uparrow, n'_\downarrow](t), \end{aligned} \quad (3.38)$$

which leads to a different ground state specified by the Kohn–Sham orbitals $\varphi'_{i,\sigma}(\mathbf{r};t)$ and their corresponding occupation number $f'_{i,\sigma}$. From now on we will denote all occupied states for a specific spin σ using indices h and h' , whereas all unoccupied states for a specific spin are denoted by p or p' . An occupied state fulfills the condition $f_{i,\sigma} > 0$. According to the theorem of Thouless [38] we can choose $\delta\varphi_{h,\sigma}(\mathbf{r};t)$ orthogonal to all occupied orbitals,

$$\delta\varphi_{h,\sigma}(\mathbf{r};t) = \sum_p \delta c_{ph,\sigma}(t) \varphi_{p,\sigma}(\mathbf{r}) . \quad (3.39)$$

and get

$$\begin{aligned} \mathcal{N}_{h,\sigma}(t) &= \sqrt{\int d^3r \left| \varphi'_{h,\sigma}(\mathbf{r};t) \right|^2} = \sqrt{\int d^3r \left| \varphi_{h,\sigma}(\mathbf{r}) \right|^2 + \int d^3r \left| \delta\varphi_{h,\sigma}(\mathbf{r};t) \right|^2} \\ &= \sqrt{1 + \int d^3r \left| \delta\varphi_{h,\sigma}(\mathbf{r};t) \right|^2} = \sqrt{1 + \sum_p |\delta c_{ph,\sigma}(t)|^2} . \end{aligned} \quad (3.40)$$

3.4.2 Linear equations of motion

To get linear equations of motion we have to expand the perturbed Lagrangian density, Eq. (3.38), to second order. After a several page long derivation, which is not included in this document, we get

$$\begin{aligned} \mathcal{L}(t) &= \sum_{h,\sigma} f_{h,\sigma} \int d^3r \int d^3r' \delta\varphi_{h,\sigma}^*(\mathbf{r};t) \left[h_{\text{ks}}^{(\sigma)}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}, \mathbf{r}') - \epsilon_{h,\sigma} \delta(\mathbf{r} - \mathbf{r}') \right] \delta\varphi_{h,\sigma}(\mathbf{r}';t) \\ &\quad + \frac{1}{2} \sum_{\sigma,\sigma'} \int d^3r \int d^3r' \delta n_{\sigma}(\mathbf{r};t) v_{\text{ph}}^{(\sigma,\sigma')}(\mathbf{r}, \mathbf{r}') \delta n_{\sigma'}(\mathbf{r}';t) + \sum_{\sigma} \int d^3r \delta v(\mathbf{r};t) \delta n_{\sigma}(\mathbf{r};t) \\ &\quad + \frac{i\hbar}{2} \sum_{h,\sigma} f_{h,\sigma} \int d^3r \left[\delta\varphi_{h,\sigma}^*(\mathbf{r};t) \delta\dot{\varphi}_{h,\sigma}(\mathbf{r};t) - \delta\dot{\varphi}_{h,\sigma}^*(\mathbf{r};t) \delta\varphi_{h,\sigma}(\mathbf{r};t) \right] . \end{aligned} \quad (3.41)$$

Here $v_{\text{ph}}^{(\sigma,\sigma')}(\mathbf{r}, \mathbf{r}')$ is the so called particle–hole potential,

$$v_{\text{ph}}^{(\sigma,\sigma')}(\mathbf{r}, \mathbf{r}') \equiv \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} + \left. \frac{\delta^2 E_{\text{xc}}}{\delta n_{\sigma}(\mathbf{r};t) \delta n_{\sigma'}(\mathbf{r}';t)} \right|_{t=0} , \quad (3.42)$$

in adiabatic approximation.

To ensure the orthogonality condition for $\delta\varphi_{h,\sigma}(\mathbf{r};t)$ we introduce $\delta\psi_{h,\sigma}(\mathbf{r};t)$ so that its projection on the unoccupied states gives $\delta\varphi_{h,\sigma}(\mathbf{r};t)$,

$$\delta\varphi_{h,\sigma}(\mathbf{r};t) = \int d^3r' P_{\sigma}(\mathbf{r}, \mathbf{r}') \delta\psi_{h,\sigma}(\mathbf{r}';t) , \quad (3.43)$$

where

$$P_{\sigma}(\mathbf{r}, \mathbf{r}') \equiv \delta(\mathbf{r} - \mathbf{r}') - \sum_h \varphi_{h,\sigma}(\mathbf{r}) \varphi_{h,\sigma}^*(\mathbf{r}') . \quad (3.44)$$

This allows us to derive the corresponding Euler–Lagrange equations by

$$\begin{aligned}
0 &= \frac{\partial \mathcal{L}}{\partial \delta \psi_{h,\sigma}^*} - \frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\delta \psi}_{h,\sigma}^*} \\
&= \int d^3 r' P_\sigma(\mathbf{r}, \mathbf{r}') \left[\int d^3 r'' \left[h_{\text{ks}}^{(\sigma)}[n_\uparrow, n_\downarrow](\mathbf{r}', \mathbf{r}'') - \epsilon_{h,\sigma} \delta(\mathbf{r}' - \mathbf{r}'') \right] \delta \varphi_{h,\sigma}(\mathbf{r}''; t) \right. \\
&\quad \left. + i\hbar \delta \dot{\varphi}_{h,\sigma}(\mathbf{r}'; t) + \varphi_{h,\sigma}(\mathbf{r}') \delta v(\mathbf{r}'; t) + \varphi_{h,\sigma}(\mathbf{r}') \sum_{\sigma'} \int d^3 r'' v_{\text{ph}}^{(\sigma, \sigma')}(\mathbf{r}', \mathbf{r}'') \delta n_{\sigma'}(\mathbf{r}''; t) \right] \\
&= \int d^3 r' \left[h_{\text{ks}}^{(\sigma)}[n_\uparrow, n_\downarrow](\mathbf{r}, \mathbf{r}') - \epsilon_{h,\sigma} \delta(\mathbf{r} - \mathbf{r}') \right] \delta \varphi_{h,\sigma}(\mathbf{r}'; t) + i\hbar \delta \dot{\varphi}_{h,\sigma}(\mathbf{r}; t) \\
&\quad + \int d^3 r' P_\sigma(\mathbf{r}, \mathbf{r}') \varphi_{h,\sigma}(\mathbf{r}') \left[\delta v(\mathbf{r}'; t) + \sum_{\sigma'} \int d^3 r'' v_{\text{ph}}^{(\sigma, \sigma')}(\mathbf{r}', \mathbf{r}'') \delta n_{\sigma'}(\mathbf{r}''; t) \right]
\end{aligned} \tag{3.45}$$

and its complex conjugate. In Laplace–space the previous expression reads

$$\begin{aligned}
0 &= \int d^3 r' \overbrace{\left[h_{\text{ks}}^{(\sigma)}[n_\uparrow, n_\downarrow](\mathbf{r}, \mathbf{r}') - (\epsilon_{h,\sigma} - i\hbar s) \delta(\mathbf{r} - \mathbf{r}') \right]}^{=: \bar{T}_{h,\sigma}(\mathbf{r}, \mathbf{r}'; s)} \delta \bar{\varphi}_{h,\sigma}(\mathbf{r}'; s) \\
&\quad + \int d^3 r' P_\sigma(\mathbf{r}, \mathbf{r}') \varphi_{h,\sigma}(\mathbf{r}') \delta \bar{v}(\mathbf{r}'; s) \\
&\quad + \int d^3 r' P_\sigma(\mathbf{r}, \mathbf{r}') \varphi_{h,\sigma}(\mathbf{r}') \sum_{\sigma'} \int d^3 r'' v_{\text{ph}}^{(\sigma, \sigma')}(\mathbf{r}', \mathbf{r}'') \delta \bar{n}_{\sigma'}(\mathbf{r}''; s).
\end{aligned} \tag{3.46}$$

3.4.3 Linear response function formulated without unoccupied orbitals

Eq. (3.46) can be cast as

$$\begin{aligned}
&- \int d^3 r' \bar{T}_{h,\sigma}^{-1}(\mathbf{r}, \mathbf{r}'; s) \int d^3 r'' P_\sigma(\mathbf{r}', \mathbf{r}'') \varphi_{h,\sigma}(\mathbf{r}'') \delta \bar{v}(\mathbf{r}''; s) = \delta \bar{\varphi}_{h,\sigma}(\mathbf{r}; s) + \\
&\quad + \int d^3 r' \bar{T}_{h,\sigma}^{-1}(\mathbf{r}, \mathbf{r}'; s) \int d^3 r'' P_\sigma(\mathbf{r}', \mathbf{r}'') \varphi_{h,\sigma}(\mathbf{r}'') \sum_{\sigma'} \int d^3 r''' v_{\text{ph}}^{(\sigma, \sigma')}(\mathbf{r}'', \mathbf{r}''') \delta \bar{n}_{\sigma'}(\mathbf{r}'''; s).
\end{aligned} \tag{3.47}$$

If we multiply with $f_{h,\sigma} \varphi_{h,\sigma}^*(\mathbf{r})$, add the complex conjugate and sum over all occupied states h we get

$$\int d^3 r' \bar{\chi}_0^{(\sigma)}(\mathbf{r}, \mathbf{r}'; s) \delta \bar{v}(\mathbf{r}'; s) = \int d^3 r' \epsilon_\sigma(\mathbf{r}, \mathbf{r}') \delta \bar{n}_{\sigma'}(\mathbf{r}'; s), \tag{3.48}$$

where

$$\epsilon_\sigma(\mathbf{r}, \mathbf{r}') \equiv \delta(\mathbf{r} - \mathbf{r}') - \int d^3 r'' \bar{\chi}_0^{(\sigma)}(\mathbf{r}, \mathbf{r}''; s) \sum_{\sigma'} v_{\text{ph}}^{(\sigma, \sigma')}(\mathbf{r}'', \mathbf{r}') \tag{3.49}$$

represents the dielectric function of the interacting system and

$$\bar{\chi}_0^{(\sigma)}(\mathbf{r}, \mathbf{r}'; s) \equiv - \sum_h f_{h,\sigma} \int d^3 r'' \left[\varphi_{h,\sigma}^*(\mathbf{r}) \bar{T}_{h,\sigma}^{-1}(\mathbf{r}, \mathbf{r}''; s) P_\sigma(\mathbf{r}'', \mathbf{r}') \varphi_{h,\sigma}(\mathbf{r}') + c.c. \right]. \tag{3.50}$$

denotes the linear spin response function of the non-interacting Kohn–Sham system. Please note that $\bar{\chi}_0^{(\sigma)}(\mathbf{r}, \mathbf{r}'; s)$ is symmetric, because $\hat{T}_{h,\sigma}$ and $\hat{P}_\sigma$ commute.

We can extract the linear response function $\bar{\chi}(\mathbf{r}, \mathbf{r}'; s)$ of the interacting system by comparing Eq. (3.48) with Eq. (3.34) and identify

$$\bar{\chi}(\mathbf{r}, \mathbf{r}'; s) = \sum_{\sigma} \bar{\chi}^{(\sigma)}(\mathbf{r}, \mathbf{r}'; s) \quad (3.51)$$

with

$$\bar{\chi}^{(\sigma)}(\mathbf{r}, \mathbf{r}'; s) = \int d^3r'' \epsilon_{\sigma}^{-1}(\mathbf{r}, \mathbf{r}'') \bar{\chi}_0^{(\sigma)}(\mathbf{r}'', \mathbf{r}'; s). \quad (3.52)$$

The most important property of $\bar{\chi}(\mathbf{r}, \mathbf{r}'; s)$ is that it does not depend on any unoccupied Kohn–Sham orbitals. Therefore, the extremely time consuming procedure of calculating an immense number of eigenvectors can be skipped. Instead, one has to apply $T_{h,\sigma}^{-1}(\mathbf{r}, \mathbf{r}'; s)$ and $\epsilon_{\sigma}^{-1}(\mathbf{r}, \mathbf{r}')$ in real-space. It is not practicable or even possible (if the number of discretization points is too big) to invert those functions directly. We use a inner/outer iteration scheme to calculate the density response. In the outer iteration loop we solve Eq. (3.48) using a biconjugate gradient stabilized (BiCGstab) method. In every iteration step one has to apply $\bar{\chi}_0^{(\sigma)}(\mathbf{r}, \mathbf{r}'; s)$, which is not known explicitly. The inner iterative solver applies $T_{h,\sigma}^{-1}(\mathbf{r}, \mathbf{r}'; s)$ to an arbitrary function. This can be accomplished very efficiently by means of a preconditioned conjugate residual (CR) method with a circulant preconditioner.

4 Model for cluster–atom interactions

From a theoretical point of view we already know how to calculate intermolecular potentials exactly; we have to solve the many–body Schrödinger equation. For very small systems this can be done using quantum chemistry methods like Coupled Cluster and Configuration Interaction, which are exact in principle. But already at that level, the numerics becomes problematic. The typical energy of a bound electron ($\sim \text{Ry}$) is a factor 10^5 larger than the typical intermolecular interaction energy ($\sim \text{K}$). Therefore, one has to have very small numerical errors in the computations.

Those methods, of course, are not an option for systems with larger numbers of electrons; larger means about 10 here. Therefore, we have to find a suitable model to describe the interactions or we have to use more elaborate methods instead of brute–force numerics. In the following sections we will discuss the important ingredients for a interaction model — the short–range and the long–range correlations — and give first preliminary results for Mg–He and Na–He potentials.

4.1 Ingredients for the interaction model

The fact that the interaction energies between neutral particles is very small compared to the electronic energies is on the one hand very problematic concerning numerics. but on the other hand it is helpful, because we can try to get good results using perturbative methods.

The only caveat is that a finite perturbation sum does not provide the correct short–range behavior. We assume that this problem does not cause larger effects than other approximations we make.

4.1.1 Repulsive part of the potential

Due to the short–range correlation we encounter a phenomenon which is widely known as Pauli repulsion. For small interparticle separations the repulsive Coulomb interaction between the electrons dominates the interparticle interaction and also exchange–effects become important. To model this situation we follow the idea of Patil [39] and calculate the direct Coulomb interaction energy between the two particles in the limit of slightly overlapping wave functions. To account for the exchange we add a correction term which only includes exchange between s –electrons. We get

$$V_{A-B}^{(\text{rep})} = \frac{4\pi}{3} n_A(\mathbf{R}_{AB}) \left[\langle r^2 \rangle_B + \frac{148}{90} \frac{\langle r^4 \rangle_B}{b_A^2(\vartheta_{AB}, \varphi_{AB})} + \frac{228}{525} \frac{\langle r^6 \rangle_B}{b_A^4(\vartheta_{AB}, \varphi_{AB})} + \dots \right]. \quad (4.1)$$

Here $\mathbf{R}_{AB} = (R_{AB}, \vartheta_{AB}, \varphi_{AB})$ is the position of the atom (indicated with B) relative to the center of mass of the cluster (indicated with A) in spherical coordinates, $n_A(\mathbf{r})$ is the

electronic density of the cluster (the center of mass of the cluster is at the origin) and $b_A(\vartheta, \varphi)$ is the decay coefficient of the cluster's electronic density for large distances from the center of mass, $n_A(\mathbf{r}) = C_A(\vartheta, \varphi)e^{-b_A(\vartheta, \varphi)r}$.

4.1.2 Attractive part of the potential

The attractive part of the interaction is usually split into two contributions. The first is the induction interaction, which is simply the static Coulomb interaction between polarizable particles and enters the perturbation sum as a second order term. In our model we assume that the changes in the electronic structure of the spherical rare gas atom are small. Therefore, we further assume that there is no external electric field caused by the atom which could induce any changes in the cluster, only the rare gas atom gets polarized. This leads to an induction potential of the form

$$V_{A-B}^{(\text{ind})}(\mathbf{R}_{AB}) = -\frac{1}{2}\alpha_B(0)\mathbf{E}^2(\mathbf{R}_{AB}), \quad (4.2)$$

where $\alpha_B(0)$ is the static polarizability of atom B and $\mathbf{E}(\mathbf{r})$ is the electric field caused by the cluster in its ground state.

The second contribution to the attractive part of the interaction is the so-called dispersion interaction. It arises due to correlation effects between the electrons — their correlated zero-point motion — and it contributes to the perturbation sum as second and higher order terms. In the long-range limit one can describe this interaction van der Waals coefficients $C_n^{(A-B)}$. A commonly used way [9] to calculate these coefficients is:

- multipole expansion of interparticle interaction W_{A-B}
- assume non-overlapping electronic densities
- $\Rightarrow$ **divergence for small interparticle distance**
- perturbation theory

In the long-range limit the dispersion interaction between neutral cluster A and neutral, spherical atom B is

$$V_{A-B}^{(\text{disp})}(\mathbf{R}_{AB}) = -\sum_{n=6}^{\infty} \frac{C_n^{(A-B)}(\vartheta_{AB}, \varphi_{AB})}{R_{AB}^6}. \quad (4.3)$$

The dynamic polarizabilities at imaginary frequency $\alpha(i\omega)$ can be used to express the leading term as [40]

$$\frac{C_n^{(A-B)}(\vartheta_{AB}, \varphi_{AB})}{R_{AB}^6} = \int_0^\infty \frac{d\omega}{2\pi} \text{Tr} \{ \alpha_A(i\omega) \cdot \Phi(\mathbf{R}_{AB}) \cdot \alpha_B(i\omega) \cdot \Phi(\mathbf{R}_{AB}) \} \quad (4.4)$$

with

$$\Phi(\mathbf{R}) = \frac{\delta_{\mu\nu}}{R^3} - \frac{3R_\mu R_\nu}{R^5}. \quad (4.5)$$

In this formula, many-body properties of the cluster enter through $\alpha(i\omega)$. For spherical clusters only even-numbered van der Waals coefficients contribute to the dispersion interaction. These coefficients can be calculated accordingly to the example above [41] using

quadrupole, octopole, ... dynamic polarizabilities in addition to the dipole dynamic polarizabilities. The odd-numbered coefficients involve quantities like the dipole-quadrupole dynamic polarizability of the cluster.

The idea now is to use published dynamic polarizabilities for the rare gas atoms and calculate the needed dynamic polarizabilities of the clusters using linear response. For example, the formula for the dipole dynamic polarizability is

$$\alpha_{\mu\nu}(\omega) = \int d^3r \int d^3r' r_\mu r'_\nu \chi(\mathbf{r}, \mathbf{r}'; \omega). \quad (4.6)$$

In the expansion proposed by [41] it is more suitable to work in a spherical harmonics basis and formulas for other dynamic polarizabilities have to be derived.

4.1.3 Combining repulsive and attractive part of the potential

The problem of simply adding $V_{A-B}^{(\text{rep})}$, $V_{A-B}^{(\text{ind})}$ and $V_{A-B}^{(\text{disp})}$ is that we assumed non-overlapping charge densities to derive $V_{A-B}^{(\text{disp})}$. Therefore, we have to deal with unphysical divergences for $R_{AB} \rightarrow 0$. This problem can be fixed by multiplying the terms in the van der Waals sum with so-called damping functions $f_n(\mathbf{R}_{AB})$ [42],

$$V_{A-B}^{(\text{damp})}(\mathbf{R}_{AB}) = - \sum_{n=6}^{\infty} f_n(\mathbf{R}_{AB}) \frac{C_n^{(A-B)}(\vartheta_{AB}, \varphi_{AB})}{R_{AB}^6}. \quad (4.7)$$

These damping functions ensure the correct qualitative behavior of the dispersion interaction. Finally, our model for the cluster-atom interaction is

$$V_{A-B}(\mathbf{R}_{AB}) = V_{A-B}^{(\text{rep})} + V_{A-B}^{(\text{ind})} + V_{A-B}^{(\text{damp})}(\mathbf{R}_{AB}). \quad (4.8)$$

At this point we want to emphasize that our potential model is not a pairwise sum model. It uses electronic properties of the cluster rather than electronic properties of its constituents.

4.2 Preliminary results for Mg-He and Na-He potentials

Figures 4.1 and 4.2 show the potential curves for Mg-He and Na-He obtained with our potential model, respectively, in comparison with results from the literature. The dispersion interaction in our model was evaluated up to C_{10} . We have chosen to present this two simple examples, because they are the only way to test and verify our model. It can then be easily applied to more complex systems.

The Mg-He interactions shown in Figure 4.1 are in good overall agreement. Please note that our simple perturbative model (red solid) gives very similar results to potentials obtained by CCSD(T) calculations, Ref. [43] (green dashed) and Ref. [44] (blue dotted). In the case of the Na-He interactions, Figure 4.2, the agreement between the different proposed energy curves is not good. The potentials calculated with multi-reference quantum chemistry methods, Ref. [44] (blue dotted) and Ref. [45] (magenta short-dotted), show the largest discrepancy, which is unexpected. Nevertheless, our potential (red solid) seems to be reasonable.

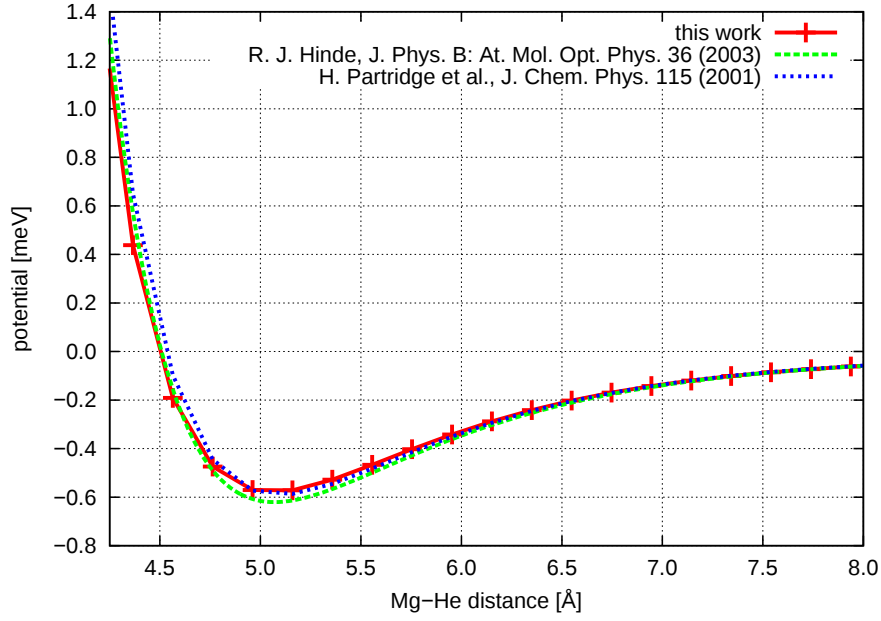


Figure 4.1: Different Mg-He potentials in comparison. The red solid curve shows the results of this work, Eq. (4.8), the green dashed curve the results of [43], the blue dotted curve the potential published in [44]. The three curves are in good agreement.

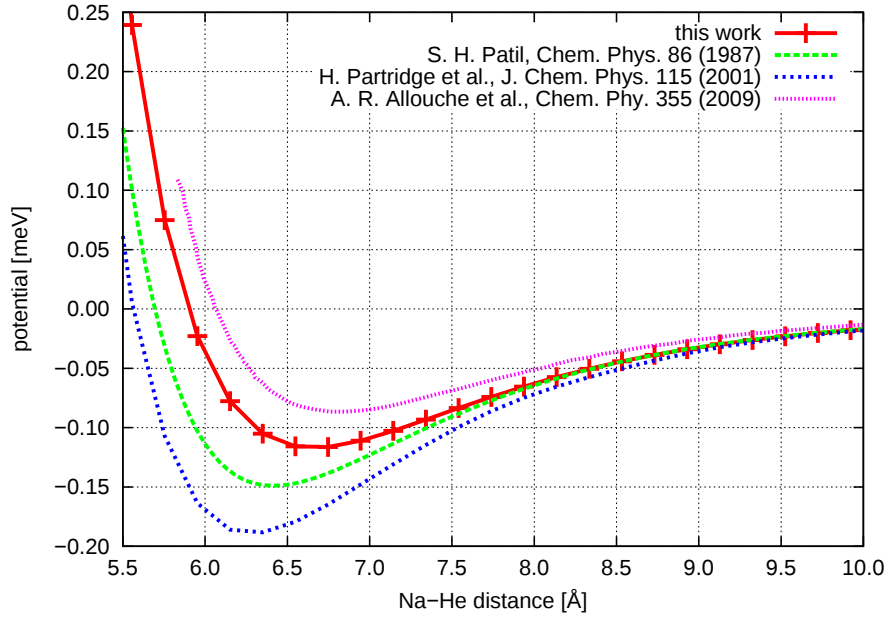


Figure 4.2: Different Na-He potentials in comparison. The red solid curve shows the results of this work, Eq. (4.8), the green dashed curve the results of [39], the blue dotted curve the potential published in [44] and the magenta short-dotted curve the results of [45]. Please note the large discrepancy between the last two references, which are both obtained by multi-reference quantum chemistry methods.

5 Conclusion and Outlook

In Chapter 2 we have presented some analytic examples which show the importance of many-body effects in physical adsorption and the flaw in pairwise sum models like the Hamaker model. This model is only applicable to surfaces which do not show curvature. It has been demonstrated that it totally fails to describe the extreme case of a spherical particle interacting with an atom at large distance. The problem is that the effective C_6 coefficients used in the Hamaker model contain information about the electromagnetic screening caused by the flat surface. This is a geometrical effect which is absent in the case of a spherical particle. We conclude that geometrical effects have to be included in any simple pairwise sum model and have proposed a method similar to Hamaker's to include many-body effects due to the chemical environment. The content of Chapter 2 is and will be published in Ref. [1] and Ref. [2], respectively.

A new linear response time-dependent density functional method has been introduced in Chapter 3. The most important property of the density-density response function $\bar{\chi}(\mathbf{r}, \mathbf{r}'; s)$ is that it does not depend on any unoccupied Kohn-Sham orbitals. Therefore, it overcomes the necessity of calculating a huge number of unoccupied states. The price one has to pay for this advantage is that one has to solve a linear equation directly in real-space. A very efficient inner/outer iteration scheme has been proposed to accomplish that. This new method is very interesting because linear response functions are widely used for many dynamic problems in physics, for example transport problems. Another promising application is the density update in density functional theory. Up to now approximate response functions were used, because the computation of many unoccupied Kohn-Sham orbitals was too expensive. With my method this is no longer a problem as the exact linear response function can be used for the density update which should drastically reduce the number of self-consistency iterations.

In Chapter 4 a simple model for cluster-atom interaction has been derived by means of perturbation theory. It uses electronic properties of the cluster rather than electronic properties of its constituents and is therefore more elaborate than pairwise sum models. This enables us to study many-body effects in van der Waals interaction and allows us to estimate when and if those effects become important. But the model also has its flaws, for example the assumption of non-overlapping charge densities for the dispersion interaction and the perturbative treatment of the short-range correlations. For a more detailed study, improvements will be necessary. One idea is to use correlated basis functions instead of a simple Kohn-Sham Slater determinant as Ansatz wave function. This will allow us to describe to correctly describe the important short-range correlations.

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