Renormalization and Universality of Van der Waals forces

Enrique Ruiz Arriola and Alvaro Calle Cordón

Departamento de Física Atómica, Molecular y Nuclear, Universidad de Granada, E-18071 Granada, Spain

Abstract. Renormalization ideas can profitably be exploited in conjunction with the superposition principle of boundary conditions in the description of model independent and universal scaling features of the singular and long range Van der Waals force between neutral atoms. The dominance of the leading power law is highlighted both in the scattering as well as in the bound state problem. The role of off-shell two-body unitarity and causality within the Effective Field Theory framework on the light of universality and scaling at low energies is analyzed.

1 Introduction

Van der Waals (VdW) forces were first conjectured from the experimental observation that in an adiabatic expansion a gas of neutral particles cools down (Joule-Thomson effect). Since the inter-particle distance at room temperature is \( \sim 30\,\text{Å} \) this suggests that VdW forces are long range and attractive. Their genuine quantum mechanical origin and form \( \sim 1/r^6 \) was uncovered by London [2] as long range dipole fluctuations between charge-neutral atomic and molecular systems. They dominate at distances above 5 – 10Å and hold atomic dimers together. The relativistic Casimir-Polder forces \( \sim 1/r^7 \) include retardation, are a consequence of vacuum fluctuations [3] and operate at very long distances \( \sim 1000 – 2000\,\text{Å} \), a relevant scale in colloids. The general field theoretical treatment due to two photon exchange [4] yielded the so far missing magnetic contribution (For a review see e.g. [5]).

Van der Waals forces, besides being long range, diverge if directly extrapolated to short distance scales but a sensible interpretation becomes possible [6,7]. Because of the interest on ultra-cold atoms in recent years [8] fundamental work for neutral atoms was initiated in Refs. [9–11] (see also [12]) from the point of view of quantum defect theory, where a spectacular reduction of parameters takes place. This is supported by more conventional potential calculations and a pattern of (VdW) universality and scaling sets in [13] with no explicit reference to short distance scales or cut-offs. Actually, Effective Field Theories (EFT) explicitly exploit the characteristic low energy parameter reduction from the start and yield very general universality patterns which do not resolve the nature of the forces and therefore enjoy a wide applicability [14–16]. They are based on pure contact (zero range) interactions and discard the long distance tail of VdW forces. In the present contribution we analyze the quantum mechanical problem from the point of view of renormalization, and address to what extent do these contact interactions faithfully describe the underlying Van der Waals force.

2 From Binding to Van der Waals forces

To provide a proper perspective it is interesting to recall the distance scales where we expect the dispersion forces to dominate. For simplicity let us consider the simplest \( \text{H}_2 \) molecule, which Hamiltonian in the CM frame and in the Born-Oppenheimer approximation, valid for heavy protons, \( m_p \gg m_e \), reads

\[
H = H_1 + H_2 + V_{12}
\]

(1)

where the single atom hydrogen-like Hamiltonians are

\[
H_{1,2} = -\frac{1}{2m_e} \nabla^2_{1,2} - \frac{\alpha}{|\mathbf{r}_{1,2} + \mathbf{r}/2|}
\]

(2)

with \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \) the electron coordinates and

\[
V_{12} = \frac{\alpha}{4|\mathbf{r}|} \left[ \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}/2|} - \frac{1}{|\mathbf{r}_2 + \mathbf{r}/2|} \right]
\]

(3)

Defining \( \mathbf{r}_{1,\pm} = \mathbf{r}_1 \pm \mathbf{r}/2 \) and \( \mathbf{r}_{2,\pm} = \mathbf{r}_2 \pm \mathbf{r}/2 \), the solutions to Eq. (2) are \( \psi_n^{(0)}(\mathbf{r}_{1,\pm}) \) and \( \psi_m^{(0)}(\mathbf{r}_{2,\pm}) \) where \( E_n = -m_e\alpha^2/2n^2 = -13.6\,\text{eV}/n^2 \) [17] so that for \( V_{12} = 0 \) the total mirror symmetric molecular normalized wave function reads

\[
\psi_{nm}^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\psi_n^{(0)}(\mathbf{r}_{1,\pm})\psi_m^{(0)}(\mathbf{r}_{2,\pm}) \pm \psi_n^{(0)}(\mathbf{r}_{1,\pm})\psi_m^{(0)}(\mathbf{r}_{2,\pm})}{\sqrt{2(1 + \delta_{nm})}}
\]

(4)

\(^2\) We work in natural units with \( \hbar = c = 1 \) and \( \alpha = e^2/(4\pi\epsilon_0\hbar c) = 1/137.04 \) the fine structure constant and \( \hbar c = 1973.2\,\text{ÅeV} \). The Bohr radius is \( a_0 = \hbar^2/(m_e\alpha) = 0.51\,\text{Å} \).
with $S_{nm}(r)$ the corresponding overlap integral, fulfilling

$$S_{n,m}(0) = \delta_{n,m}$$

and $S_{n,m} = O(e^{-2r/a_0})$. This generates a coupled channel matrix Hamiltonian what eigenvalues provide

$$E_{\text{H-H}}(r) \rightarrow 2E_\text{H} \text{ for } r \rightarrow \infty$$

The nowadays standard variational approach pioneered by Heitler and London [18] and culminating with the benchmark determination of the ground state dissociation energy [19] does not accurately work at very long distances, and thus perturbation theory might be preferable. Taking $H_0 = H_1 + H_2$ as the unperturbed Hamiltonian and $V_{12}$ as the perturbation, one can determine the potential energy shift of the system at a fixed proton-proton separation $r$ in perturbation theory, which to second order reads,

\begin{equation}
V_{\text{H-H}}(r) = E_{\text{H-H}}(r) - 2E_\text{H} = \Delta E_1(r) + \Delta E_2(r) + \ldots \tag{5}
\end{equation}

In the case of the $H_2$ molecule the calculation was undertaken in 1930 by London and Eisenschitz [20] in the closure approximation (CA) \footnote{This somewhat crude approximation corresponds to replace

$$\sum_{n \neq 0} \frac{|V_{00}|^2}{E_n - E_0} = \frac{(V^2)_{0,0} - V_{0,0}^2}{E_1 - E_0}$$

Note that the sum includes also continuum $e - p$ states.}. We have reproduced the analytical calculation [21] and the results are presented in Fig. 1. Already in $\Delta E_1(r)$ the finite atomic size effects which are $\sim e^{-2r/a_0}$.

An interesting feature is that due to the finite atomic size, $\sim a_0$, second order in perturbation theory is finite at zero separation, $|\Delta E_2(0)| < \infty$. Actually, for $r \rightarrow 0$ we expect the exact behaviour $V_{\text{H-H}}(r) - \alpha/r \rightarrow E_{\text{He}} - 2E_\text{H}$. In the CA we get $E_{\text{He}}^{\text{CA}} = -110$eV to be compared with $E_{\text{He}}^{\text{exact}} = -79$eV. At large distances only the second order direct term in Eq. (5) contributes yielding,

\begin{equation}
V(r) = -\sum_{n \neq 0} \frac{C_n}{r^n} + O(e^{-r/a_0}) \tag{6}
\end{equation}

where in the CA $C_n = -c_n m_c a^2 \alpha^2 \phi_0^2$ with $c_6 = 6$, $c_8 = 135$, $c_{10} = 7875/2$, about 5% accurate compared to exact values (see table 1). For $n \gg 6$ one has $C_n \sim (a_0)^n n!$ which means that the VdW series represents a diverging asymptotic expansion. As it usually happens in such a case, for a fixed order of the truncation, this poses a lower limit on the distance below which it makes no sense improve the calculation. Usually, only the terms with $n = 6, 8, 10$ are retained. \footnote{See e.g. the impressive calculation in Hydrogen up to $C_{12}$ [22] for which we can fit a behaviour $C_n \sim (1/2)^n n!$ in atomic units. In the CA we have $C_{12}^{\text{CA}} = 1.93 \times 10^{26}$ to be compared with $C_{12}^{\text{exact}} = 2.51 \times 10^{26}$ [22].}

Calculations show that, so far, corrections are always negative, i.e. $C_n > 0$ as could be inferred from the Lieb-Thirring universal bound [23] which establishes that generally $V(r) < -c/r^6$ for any pair of atoms with underlying Coulomb forces such as in Eq. (2). The positivity of the $C_n$‘s will prove essential in what follows. As we see in Fig. 1 in the $H_2$ case the Van der Waals force dominates for distances of about 5Å. Actually this corresponds to an accuracy $O(e^{-r/a_0})$, and the coupled channel Hamiltonian reads

\begin{equation}
H_{\text{He,He};n,m} = (E_n + E_m)\delta_{n,m} + V_{\text{He,He}}(r) \tag{7}
\end{equation}

This problem may quite generally be decomposed within the total multichannel Hilbert space into the $P$-space (elastic) and $Q$-space (excited) states [25], where $P = (0,0)/0$ and $Q = 1 - P$ are the corresponding projection operators. This yields the box-matrix structure

\begin{align*}
H_{PP} \Psi_P + V_{PQ} \Psi_Q & = E \Psi_P \\
V_{QP} \Psi_P + H_{QQ} \Psi_Q & = E \Psi_Q 
\end{align*}

where in the Born-Oppenheimer approximation all these potentials are local functions of the inter-nuclear separation $r$. Eliminating the unobserved channels we get the effective optical potential

\begin{equation}
\tilde{V}_{PP}(E) = V_{PP} + V_{PQ}(E - H_{QQ})^{-1} V_{QP} \tag{9}
\end{equation}

which develops an imaginary part if the first inelastic threshold becomes open. The important point is that if the complete underlying electronic Hamiltonian, Eq. (1) is energy independent, then for $E = p^2/2\mu + 2E_\text{H} < E_{\text{He}} + E_\text{H}$

\begin{equation}
\tilde{V}_{PP}(E) = -V_{PQ}(E - H_{QQ})^{-2} V_{QP} < 0 \tag{10}
\end{equation}
The underlying local and energy independent dynamics has consequences in the low energy EFT representations of the VdW interactions (see Section 6).

3 Universal Scaling Theorems

We review here some results found in a previous work [26, 27] (for a short review see e.g. [28]), within a nuclear physics and multichannel context which will prove useful in the analysis of VdW forces. Our starting point is the finite energy scattering state Schrödinger’s equation for the relative wave function between two particles of masses $m_1$ and $m_2$ which interact through a central potential,

$$-u'' + U(r)u + \frac{l(l + 1)}{r^2}u = k^2 u,$$

(11)

where $U(r) = 2\mu V(r) / \hbar^2$ is the reduced mass, $k = p / \hbar = 2\pi / \lambda$ the wavenumber and $u(r)$ the reduced wave function. We will neglect finite size and exchange effects and take $V(r)$ given just by Eq. (6) where $C_n$ are the standard VdW coefficients which are computed $ab initio$ from electronic orbital atomic structure calculations [29]. The potential in Eq. (6) can conveniently be rewritten as

$$U(r) = -\frac{R_0^2}{r^6} \left[ 1 + g_1 r^2 + g_2 r^4 + \ldots \right].$$

(12)

where $R_0 = (2\mu C_0)^{1/6}$ is the VdW length scale and $g_1, g_2, \ldots$ represent the contributions from $C_8, C_{10}$ etc. at $r = R_0$ respectively. In Table 1 we compile numbers for a bunch of interesting cases. Typically, $R_0 \sim 10 - 200\text{Å}$ but also $g_1 \sim 10^{-2}$ and $g_2 \sim 10^{-4}$. This immediately the question under what conditions the expansion (12) can be truncated in a meaningful way, i.e. when the neglected terms can indeed be considered negligible in scattering and bound state properties. This question is intriguing since at short distances the more singular terms are manifestly more divergent. Actually, the range where $C_8$ yields an important correction but $C_{10}$ is still small is $g_1^{1/4} \ll r / R_0 \ll g_1^{1/2}$ which in view of Table 1, $g_2 \sim g_1^2$, becomes extremely narrow or inexistent.

To determine the solution of Eq. (11) it is necessary to give sensible boundary conditions at the origin and infinity. For the usual regular potentials there are a regular and irregular solution at the origin, and the regularity condition $u(0) = 0$ fixes uniquely the solution. However, since the potential is singular and attractive there are two linearly independent solutions, so regularity at the origin does not select a unique solution. Indeed, at short distances the De Broglie wavelength is slowly varying, $d[U(r)]^{-1/2} / dr \ll 1$ and hence a WKB approximation holds [6, 7], yielding for $r \to 0$

$$u_k(r) \to C \left( \frac{r}{R_n} \right)^{n/4} \sin \left[ \frac{2}{n - 2} \left( \frac{R_n}{r} \right)^{n-1} + \varphi_k \right],$$

(13)

where $R_n = (2\mu C_n)^{1/(n-2)}$ corresponds to the highest VdW scale considered in Eq. (6) (see also Eq. (12). The phase $\varphi_k$ is arbitrary and could, in principle, be energy dependent (see below).

To fix ideas we will restrict to $l = 0$, $s$–waves. For a positive energy scattering state it is convenient to use the normalization at very long distances given by

$$u_k(r) \to \frac{\sin(kr + \delta_0)}{\sin \delta_0} = \cos(kr) + k \cot \delta_0 \frac{\sin(kr)}{k},$$

(14)

where $\delta_0(k)$ is the scattering phase shift for the $l = 0$ angular momentum state. For the potential which at long distances behave as Eq. (12) one has the effective range expansion (ERE) [36]

$$k \cot \delta_0(k) = -\frac{1}{\alpha_0} + \frac{1}{2} r_0 k^2 + v_2 k^4 \log(k^2) + \ldots$$

(15)

where $\alpha_0$ is the scattering length, and $r_0$ is the effective range. $\alpha_0$ and $r_0$ can be calculated from the asymptotic behaviour of the zero energy solution

$$u_0(r) \to 1 - r / \alpha_0,$$

(16)

and using the definition

$$r_0 = 2 \int_0^\infty dr \left[ (1 - r / \alpha_0)^2 - u_0(r)^2 \right].$$

(17)

Next, we use the superposition principle of boundary conditions and write

$$u_k(r) = u_{k,c}(r) + k \cot \delta_0 u_{k,s}(r),$$

(18)

with $u_{k,c}(r) \to \cos(kr)$ and $u_{k,s}(r) \to \sin(kr) / k$ for $r \to \infty$. At zero energy we have

$$u_0(r) = u_{0,c}(r) - u_{0,s}(r) / \alpha_0,$$

(19)

with $u_{0,c}(r) \to 1$ and $u_{0,s}(r) \to \sin r$ for $r \to \infty$. The short distance phase $\varphi_0$ can be fixed in practice introducing a short distance cut-off, $r_c$. The way to proceed is as follows. Given a scattering length $\alpha_0$ as input one integrates from in large down to small distances, say $r = r_c \ll R_0$ whence determining $\varphi_0$. To determine $\varphi_k$ we do the same but for finite energy states. A relation between both short distance phases can be found as follows [26]. If we build $(u_k^* u_0 - u_k u_0^*)^1$ and integrate from $r_c$ to infinity and use Eq. (18) and Eq. (19) respectively, one gets

$$\frac{1}{R_n} \sin(\varphi_k - \varphi_0) = k^2 \int_0^\infty dr \left[ u_{0,c}(r) - \frac{1}{\alpha_0} u_{0,s}(r) \right] \times \left[ u_{k,c}(r) + k \cot \delta_0(k) u_{k,s}(r) \right] ,$$

(20)

which becomes an orthogonality relation if and only if $\varphi_k = \varphi_0$. This implies that the corresponding Hamiltonian, although unbounded from below becomes self-adjoint on the domain of square integrable functions which have the short distance behaviour, Eq. (13), with the same short distance phase (a common domain of definition). In other words, the short distance common phase, $\varphi$, labels the particular self-adjoint extension of the Hamiltonian depending on the Van
Table 1. Reduced di-atomic masses, Van der Waals dispersion coefficients $C_6$, $C_8$ and $C_{10}$ as well as the leading Van der Waals length scale $R_0 = (2\mu C_6)^{1/4}$, and the dimensionless coefficients $g_1$ and $g_2$ defined by the dimensionless reduced potential $2\mu V(r)R_0^6 = -x^{-6} \left[ 1 + g_1 x^{-2} + g_2 x^{-4} + \ldots \right]$ with $x = r/R_0$, the distance in Van der Waals units, of the di-atomic systems used in the present paper. Atomic units are used throughout. The atomic masses have been taken from the National Institute of Standards and Technology http://physics.nist.gov/PhysRefData/Compositions/

<table>
<thead>
<tr>
<th>Atoms</th>
<th>$\mu$(a.u.)</th>
<th>$C_6$(a.u.)</th>
<th>$C_8$(10^4 a.u.)</th>
<th>$C_{10}$(10^6 a.u.)</th>
<th>$R_0$(a.u.)</th>
<th>$g_1(10^{-2})$</th>
<th>$g_2(10^{-4})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-Li</td>
<td>6394.697</td>
<td>1389. [31]</td>
<td>0.834 [32]</td>
<td>0.735 [32]</td>
<td>64.9214</td>
<td>1.42458</td>
<td>2.97874</td>
</tr>
<tr>
<td>Cs-Cs</td>
<td>121135.907</td>
<td>6851. [31]</td>
<td>10.200 [32]</td>
<td>15.900 [32]</td>
<td>201.8432</td>
<td>0.36544</td>
<td>0.13983</td>
</tr>
<tr>
<td>Fr-Fr</td>
<td>203270.053</td>
<td>5256. [31]</td>
<td>6.648 [33]</td>
<td>10.699 [33]</td>
<td>215.0006</td>
<td>0.27362</td>
<td>0.09526</td>
</tr>
<tr>
<td>Li-Na</td>
<td>9798.954</td>
<td>1467. [31]</td>
<td>0.988 [32]</td>
<td>0.916 [32]</td>
<td>73.2251</td>
<td>1.25605</td>
<td>2.17183</td>
</tr>
<tr>
<td>Na-K</td>
<td>26356.596</td>
<td>2447. [31]</td>
<td>2.240 [32]</td>
<td>2.530 [32]</td>
<td>106.5708</td>
<td>0.80600</td>
<td>0.80155</td>
</tr>
<tr>
<td>Na-Rb</td>
<td>32978.812</td>
<td>2683. [31]</td>
<td>2.660 [32]</td>
<td>3.130 [32]</td>
<td>115.3377</td>
<td>0.74528</td>
<td>0.65923</td>
</tr>
<tr>
<td>Cr-Cr</td>
<td>47340.881</td>
<td>733. [35]</td>
<td>0.750 [35]</td>
<td>–</td>
<td>91.2731</td>
<td>1.22821</td>
<td>–</td>
</tr>
</tbody>
</table>

The energy independence can also be deduced from the smallness of the wave function at small distances. The obvious conditions $\mathcal{A}(0) = \mathcal{D}(0) = 0$ and $\mathcal{B}(0) = \mathcal{C}(0) = 1$ are satisfied. The limiting procedure poses no problem in principle, and the divergence of the potential at short distances has been eliminated by demanding a finite physical scattering length. This is equivalent to a renormalization condition at zero energy. We will analyze below other alternative renormalization conditions based on one bound state. The effective range is defined by Eq. (17), and using Eq. (19) we get

$$r_0 = A + \frac{B}{a_0} + \frac{C}{a_0^2},$$

(26)

where

$$A = 2 \int_0^\infty dr (1 - u_{0,s}^2),$$

(27)

$$B = -4 \int_0^\infty dr (r - u_{0,s}^s u_{0,s}^s),$$

(28)

$$C = 2 \int_0^\infty dr (r^2 - u_{0,s}^s),$$

(29)

depend on the potential parameters only. The interesting feature of the previous equations is that all explicit dependence on the scattering length $a_0$ is displayed by Eq. (26). This is a universal form of a low energy theorem, which applies to any potential regular or singular at the origin which falls off faster than $1/r^4$ at large distances. Since the potential is known accurately at long distances we can visualize Eq. (26) as a long distance (VdW) correlation between $r_0$ and $a_0$.5
The above results for the effective range and phase-shift, Eq. (26) and Eq. (21) are completely general. If, in addition, the reduced potential depends on a single scale $R$, i.e. $U(r) = -F(r/R)/R^2$, one gets universal scaling relations

$$r_0 = \frac{A + B}{R} + \frac{C}{\alpha_0^2},$$

and

$$R k \cot \delta_0(k R, \alpha_0/R) = \frac{\alpha_0 A(k R) + R B(k R)}{\alpha_0 C(k R) + R D(k R)},$$

where $\bar{A}, \bar{B}$ and $\bar{C}$ are purely geometric numbers, and $\bar{A}, \bar{B}, \bar{C}$ and $D$ are functions which depend solely on the functional form of the potential. Thus, if a potential has a single scale the phase-shift can be computed once and forever for a given energy. This allows to compare quite different physical systems which have identical long range forces but different short distance dynamics. A remarkable consequence of Eq. (30) is that if $\alpha_0 \gg R$ then $r_0 \sim R$ whereas $\alpha_0 \ll R$ implies $r_0 \gg R$.

4 The Pure $-1/r^6$ VdW force

For the pure $1/r^6$ case one has an analytical solution for the zero energy state so that the effective range can be computed analytically [10, 11] using Eq. (17) to get

$$A = \frac{16 \Gamma \left(\frac{3}{2}\right)^2}{3\pi}, \quad B = \frac{4}{3}, \quad \bar{C} = \frac{4 \Gamma \left(\frac{3}{2}\right)^2}{3\pi},$$

in agreement with the general result, Eq. (30). In Fig. 2 we confront the prediction for the effective range to the result of many ab initio calculations. As we see the agreement is rather impressive, meaning that for many practical purposes Eq. (32) and Eq. (30) summarize the relevant information on the, about a hundred, data. In Fig. 3 we show the VdW universal functions $\bar{A}(k), \bar{B}(k), \bar{C}(k)$ and $D(k)$ uniquely determined by the VdW potential and which need that the scattering length be specified separately to obtain the phase shift (see Eq. (31)).

One important issue has to do with the cut-off dependence. From a Callan-Symanzik renormalization group type argument one has [27]

$$\frac{d\delta(k, r_c)}{dr_c} = -k^2 \left(\frac{u_0(r_c, r_c)}{k}\right)^2$$

when $\alpha_0$ is fixed. This in turn means that for $U(r) \sim -R^6/r^6$ and using $u_0(r_c, r_c)/k \sim (r_c/R_0)^3/k$ one has that finite cut-off corrections scale as

$$\delta(k) \sim \delta(k, r_c) = O(k^3 R^4/R_0)$$

Thus, the short distance cut-off $r_c$ is a parameter for $k R_0 \gg 1$ but becomes innocuous otherwise when $r_c \ll R_0$ implying that universality is robust. We show for a sample case in

Fig. 2. The VdW universal effective range in units of the VdW radius $R$ defined by $2\mu V(r) = -R^6/r^6$. Compared to several calculations [37] (Li-Li,Na-Na), [38] (Na-Na), [39] (Cs-Cs), [40] (Cs-Cs), [41] (Na-Rb), [42] (Be-Be), [43] (Cs-Rb), [44] (Cr-Cr), [45] (Fr-Fr), [46] (H-H), [47] (H-H), [48] (H-H), [49] (H-H).

Fig. 4 the phase shifts for fixed energies, where the rather smooth converging pattern can be clearly confirmed.

Turning to the negative energy bound states with $E = -\hbar^2 \gamma^2/(2\mu)$, the behaviour at long distances is

$$u_\gamma(r) \rightarrow \lambda e^{-\gamma r}$$

whereas at short distances the energy dependent boundary condition, Eq. (13), holds. Orthogonality to the zero energy state requires that

$$\alpha_0 = \frac{\int_0^\infty du_\gamma(r)^* u_{0,\gamma}(r)}{\int_0^\infty dr u_\gamma(r) u_{0,\gamma}(r)}$$

This relation explicitly yields the scattering length from a given bound state. Inverting the formula we get, the energy spectrum, $E_n = -\hbar^2 \gamma^2/(2\mu)$ for a fixed value of the scattering length and a fixed potential $6$. This relation determines

$$n + c = \left[\frac{1}{2\pi} + \frac{3\Gamma \left(\frac{3}{2}\right)^2}{8 \sqrt{\pi} \Gamma (\frac{5}{2})} (\gamma R)^2\right]^{\frac{1}{2}} = 0.20587(\gamma R)^{\frac{1}{2}}$$

where $c$ is a constant of order unity. Thus if we happen to have a zero energy state, $\gamma_0 = 0$ then $c = 0$ and the bound states are $E_n = -116.08n^3 \hbar^2/(2\mu R^2)$ counting downward in the spectrum.

6 Using the WKB method one obtains (see also Ref. [27])
the energy spectrum $E_n$ from the scattering length $\alpha_0$ and the potential. Conversely, we can get the scattering length $\alpha_0$ from a given bound state wave number $\gamma$. In Fig. 5 we display the lowest bound states as functions of $\alpha_0$ for the pure VdW potential in scaled units. Such an universal plot allows also to deduce the scattering length from the knowledge of the weakly bound states in a complete model independent way.

We may ask how should the neglected higher order $1/r^3, 1/r^6$, etc. terms in the potential affect the lowest order $1/r^6$ calculation. To this end we show in Fig. 6 the effect of adding the term $1/r^6$ to the potential, see Eq. (12), in the $s$-wave phase shift fixing the scattering length $\alpha_0$ to the same value. In view of the rather small $g_1 \sim 10^{-2}$ values listed in table 1 we expect tiny corrections at even large energies $kR_6 \sim 10$. This result not only shows a clear dominance of the leading dispersion coefficient $C_6$ but also that scaling of VdW forces holds beyond naive dimensional estimates, $kR_6 \approx 1$. This raises the question on the usefulness of including higher order dispersion coefficients such as $C_8$ and $C_{10}$ since the region where they can distinctly be disentangled without entering the finite size regime is extremely narrow. This is also seen in the bound state spectrum displayed in Fig. 5 since for $\gamma R_6 < 10$ a rather tiny energy shift is observed in the closest states to the continuum.

5 Phenomenological potentials

In our way of treating the renormalization of VdW forces, we need not specify the value of the scattering length, $\alpha_0$, since it exactly factors out in the expression for the phase shift (see Eq. (31)). However, to predict scattering phase shifts a particular value of $\alpha_0$ must be used. It is interesting to analyze the results from a comparative perspective with the so called realistic inter-atomic potential models, which aim at a description through the entire range of distances. Thus, one can deduce from those the value of the scattering length $\alpha_0/R_0 \approx 0.335$.
a well accepted form in terms of a few parameters, say $C_6$, $C_8$, $C_{10}$ which, in principle, can be evaluated from ab initio atomic structure electronic wave functions.

Most modern inter-atomic potentials include the asymptotic Van der Waals long distance behaviour. They are generally written as the sum of a long range dispersive term and a short distance term with a core which reflects the impenetrability of two atoms. To keep the discussion as simple as possible in terms of the number of parameters, and for illustration purposes, we will analyze the venerable Lennard-Jones potential, which we write as

$$2\mu V_{LJ} = U_{LJ}(r) = \frac{1}{R_6^6} \left[ g^6 \left( \frac{R_6}{r} \right)^{12} - \left( \frac{R_6}{r} \right)^{6} \right]$$

where we have chosen to scale the potential in the long distance VdW units $R = R_6 = (2\mu C_6)^{1/6}$. The value of the dimensionless constant $g$ determines the classical turning point $U_{LJ}(gR_6) = 0$. In these form the minimum of the potential is at $r_{\min} = 2^1 R_6$ and $U_{\min} = -1/(4g^2R_6^2)$. A relevant dimensionless parameter is the total number of bound states, which obviously increases as the repulsive term is shifted towards the origin. Within a WKB approximation the number of bound states is given by

$$N_{WKB} = \frac{1}{\pi} \int_{a}^{\infty} dr \sqrt{-U_{LJ}(r)} = \frac{0.1339}{g^2},$$

where $a = gR_6$ is the zero energy classical turning point. For $g = 0.0365$ we get $N_{WKB} = 100$, for $g = 0.0517491$ we get $N_{WKB} = 50$ and for $g = 0.115715$ we get $N_{WKB} = 10$.

Using the VdW scaled units one can predict the scattering length $a_0$ from the LJ potential and the phase shifts unambiguously for any value of $g$. The result is displayed in Fig. 7. According to Levinson’s theorem any time the scattering length jumps from $-\infty$ to $+\infty$ a new bound state diverges from the continuum into the negative energy spectrum. In Fig. 7 we display the effective range as given by Eq. (17). The divergent values of $r_0$ correspond, according to our low energy theorem, to points where the scattering length goes through zero. The very strong sensitivity to the precise location of the position of the core is manifest. In Fig. 7 we compare the universal and renormalized VdW effective range formula with the actual values deduced from the Lennard-Jones potential for a different number of bound states $N = 1, 5, 15$. The minima in the curve corresponds to a value of the scattering length passing from $-\infty$ to $+\infty$ which corresponds to entering a new bound state in the spectrum. As one sees in the LJ case there is a multivalued function reflecting the multiple branches already observed in Fig. 7. The rather universal pattern of this figure is striking because it explicitly shows that to very small uncertainties the value of the scattering length largely determines the value of the effective range, regardless on the precise number of bound states. The only remarkable exception corresponds to the case with no bound states where the zero energy turning point is located at increasingly large distances.

In a sense these correspond to almost low energy identical situations, where additional bound states are hosted by the potential as the short range repulsion is displaced towards the origin. Moreover, one expects that the largest discrepancies from renormalized VdW and LJ should take place in the case of large scattering lengths, since a larger sensitivity to short distances is displayed in such a case. Actually, this is what happens. We note that there is a relative constant shift between $r_0^0$ and $r_0^VdW$ of about $0.5 - 1.0$ for $|a_0| > 10R_6$. However, the renormalized theory works better the larger the number of bound states and also for small scattering lengths, since as we discussed in the previous section for $a_0 \gg R_6$ large distances dominate. A relevant question is whether renormalization theory as explained above can account for the behaviour of the phase shifts in a energy region where the De Broglie wavelength is larger than the short distance $kR_6 \gg 1$ provided the scattering length $a_0$ is the same. The result is shown in Fig. 8 for a variety of values of $g$ which cover several cases with large and small scattering lengths as compared to the VdW radius. We see the anticipated similarity despite the fact that both potentials are completely different at short distances. Actually, the phase-shifts are indistinguishable for $kR_6 \ll 1$, but they go hand in hand far beyond this expected region; what matters is $kR_{6d} \ll 1$. On the other hand, the ERE given by Eq. (15) truncated to second order, i.e. taking $\nu_2 = 0$ only works for $kR_6 \ll 1$. In a sense this is equivalent to “seeing” the Van der Waals force in a scattering experiment. The point of renormalization theory is

![Fig. 7](https://via.placeholder.com/150)

**Fig. 7.** (Upper panel) The scattering length $a_0$ and effective range $r_0$ of the Lennard-Jones potential as a function of the zero energy turning point $gR_0$ (in VdW units). (Lower panel) The effective range $r_0$ of the Lennard-Jones model as a function of the inverse scattering length $1/a_0$, compared to the universal renormalized VdW formula (in VdW units) for different number of bound states $N = 1, 5, 15$. 

![Fig. 8](https://via.placeholder.com/150)
that it yields model independent results and hence any
discrepancy with data can be clearly attributed to a deficient
incorporation of the long distance physics.

6 The Effective Field Theory and its limits

At very low energies the interaction between neutral atoms
can be handled by an effective range expansion, Eq. (15),
where the long range character of the VdW potential be-
comes manifest in the third term of the expansion. How-
ever, if only the first two terms are retained

\[ k \cot \delta_0(k) = -\frac{1}{\alpha_0} + \frac{1}{2} r_0 k^2, \]

there arises the interesting possibility of universally repre-
senting long range forces on equal footing with short range
interactions. We may judge the quality of such an appeal-
ing approximation by comparing Fig. 8 the result of the
renormalized VdW theory with the ERE. As we see the
expansion truncated to second order breaks down at low
energies, namely \( k R_0 \ll 1 \), as expected.

Under these very restrictive conditions the problem can be
advantageously treated by using EFT methods, which
are based on the compelling idea that at such long wave-
lengths atoms behave as elementary structureless particles.
This point of view has been stressed recently (see e.g. [14,
15]) with particular fruitful predictions in the three-bod-
ying approximation by comparing Fig. 8 the result of the
renormalized VdW theory with the ERE. As we see the
expansion truncated to second order breaks down at low
energies, namely \( k R_0 \ll 1 \), as expected.

Under these very restrictive conditions the problem can be
advantageously treated by using EFT methods, which
are based on the compelling idea that at such long wave-
lengths atoms behave as elementary structureless particles.
This point of view has been stressed recently (see e.g. [14,
15]) with particular fruitful predictions in the three-bod-
ying approximation by comparing Fig. 8 the result of the
renormalized VdW theory with the ERE. As we see the
expansion truncated to second order breaks down at low
energies, namely \( k R_0 \ll 1 \), as expected.

Under these very restrictive conditions the problem can be
advantageously treated by using EFT methods, which
are based on the compelling idea that at such long wave-
lengths atoms behave as elementary structureless particles.
This point of view has been stressed recently (see e.g. [14,
15]) with particular fruitful predictions in the three-bod-

Fig. 8. The Lennard-Jones s-wave phase shifts \( \delta_0(k) \) (in radians) for different number of bound states \( N = 0, 1, 3, 5 \) as a function of the wave number (points) compared with the corresponding VdW renormalized ones having the same scattering length \( \alpha_0 \) (solid). We compare also with the effective range expansion truncated to second order \( k \cot \delta_0(k) = -1/\alpha_0 + r_0 k^2/2 \) (dots).
space cut-off $\Lambda$ (see e.g. Ref. [51] and references therein)
\begin{equation}
\frac{1}{\alpha_0} = \frac{10(C_2M^3 - 3)^2}{9M\pi(-C_1^2M^5 + 5C_0)} - \frac{2\Lambda}{\pi}, \quad (42)
\end{equation}
and
\begin{equation}
\frac{1}{2}r_0 = \frac{50C_2(3 + C_2M^3)^2(6 + C_2M^3)}{27\pi(-5C_0 + C_2^2\Lambda^2M^2)} + \frac{2}{\pi\Lambda}. \quad (43)
\end{equation}
This leads for any cut-off $\Lambda$ to the mapping $(\alpha_0, r_0) \rightarrow (C_0, C_2)$. Eliminating $C_0$ and $C_2$ in favour of $\alpha_0$ and $r_0$, the phase shift becomes
\begin{equation}
\rho \cot\delta(p) = -\frac{2\Lambda}{\pi\alpha_0} \frac{(\pi - 2\alpha_0^2)}{2\alpha_0(\pi - 2\alpha_0) + \alpha_0^2p^2(r_0\pi\Lambda - 4)} - \frac{2\Lambda}{\pi} + \frac{p}{\pi} \log \frac{\Lambda + p}{\Lambda - p}, \quad (44)
\end{equation}
which is a real quantity for $p < \Lambda$, meaning that two-body unitarity is fulfilled. However, one has complex solutions for $C_0$ and $C_2$ if
\begin{equation}
\alpha_0^2r_0\pi\Lambda^3 - 16\alpha_0^2\Lambda^2 + 12\alpha_0\pi\Lambda - 3\pi^2 \leq 0. \quad (45)
\end{equation}
which means that the effective Lagrangian, Eq. (40), becomes non hermitian $\mathcal{L}'(x) \neq \mathcal{L}(x)$. On the other hand, it is well known that three-body unitarity rests on off-shell two-body unitarity [52], a condition which cannot be met if the interaction is not hermitian, mainly because Schwartz’s principle. So the lesson is that while a complex two-body potential may fulfill on-shell two-body unitarity, a violation of three body unitarity is still possible [51].

Generally, Eq. (45) imposes a limit on the maximum value of the cut-off $\Lambda$, but to find it we need to know both $\alpha_0$ and $r_0$. For our case of VdW interactions we have seen that the universal formula for $r_0$ in terms of $\alpha_0$, Eq. (32) works extremely well if we judge by Fig. 2. Thus, if we merge Eq. (45) equal to null and Eq. (32) we obtain a boundary in the $(\Lambda, \alpha_0)$ plane which is suitably represented in Fig. 9. Essentially and up to minor variations the meaning is that the cut-off $\Lambda$ cannot exceed the VdW wave number, $\Lambda < \pi/(2R_0)$. This issue is relevant for three-body calculations [53,54] as addressed recently [55].

The analysis of the problem in coordinate space assuming an effective local and energy independent long distance dynamics and an energy dependent boundary condition at short distances have been analyzed in Ref. [26] for s-waves and in Ref. [56] in the three-dimensional case. It is found that the locality condition for an s-wave implies
\begin{equation}
\frac{d}{dk^2} \left[ \frac{u_s(kr_c)}{u_s(kr_c)} \right] = \frac{\int_0^{r_c} u_s(kr)^2 dr}{u_s(kr_c^2)} \leq 0 \quad (46)
\end{equation}
where $u_s(kr)$ is the wave function for $r \leq r_c$. Note the resemblance with Eq. (10). If there would be no interaction for $r > r_c$, then we have
\begin{equation}
u_s(kr) = \sin (kr + \delta_0(k)), \quad r > r_c, \quad (47)
\end{equation}
which can be matched to the inner $r < r_c$ region yielding
\begin{equation}
\frac{d}{dk^2} \left[ k \cot (kr_c + \delta_0(k)) \right] \leq 0, \quad (48)
\end{equation}
this is equivalent to Wigner’s causality condition [57], as noted in [58], and combined to the ERE, Eq. (39), provides a constraint on the effective range
\begin{equation}
r_0/(2r_c) \leq 1 - r_c/\alpha_0 + r_c^2/(3\alpha_0^2). \quad (49)
\end{equation}
If there is no potential for $r > r_c$ and take $r_0 = r_{VDW}$ we get a universal lower limit for $r_c$. A similar conclusion has been presented recently [59]. The conditions featuring causality in coordinate space as well as off-shell unitarity in momentum space are depicted in Fig. 9, and suggest that modelling a finite range of VdW forces by an effective Lagrangian such as Eq. (40) requires assuming a cut-off distance larger than the VdW length.

7 Conclusions

Renormalization ideas can profitably be exploited in conjunction with the superposition principle of boundary conditions in the description of model independent and universal features of the VdW force. Our main points are

- Van der Waals interactions between neutral atoms obey scaling rules which allow to determine the scattering and binding properties universally. They are well satisfied phenomenologically and extend much beyond low energy approximations such as the effective range expansion.
- There is a clear dominance of the leading $C_6$ contribution in a rather wide energy range. The range where higher order corrections due to $C_8$ or $C_{10}$ provide a distinct correction yet the finite size effects can still be neglected is extremely narrow or nonexistent.
- Van der Waals potentials can be represented by short distance contact interactions under restrictive conditions based on causality and off-shell unitarity which are independent on the value of the scattering length. It is inconsistent to model VdW forces assuming a cut-off distance smaller than the VdW length.

We thank M. Pavón Valderrama and R. González Férez for discussions. Work supported by Spanish DGI and FEDER.
funds with grant FIS2008-01143, Junta de Andalucía grant FQM-225-05, EU Integrated Infrastructure Initiative Hadron Physics Project contract RII3-CT-2004-506078.

References