Dipole–dipole interaction between Rydberg atoms

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Abstract. The applicability of the van der Waals potential approximation ($C_6/R^6$) is limited by its smallness in comparison with the distance to the nearest undisturbed level of the system of two interacting atoms. It is shown that this condition should be taken into account in the study of interaction of Rydberg atoms. The calculation of the interaction potential for one of $\Delta$-term system of two $^7\text{Li}$ atoms in the 5d state is given. It is shown that at the violation of the specified conditions, the dependence of the potential $1/R^6$ is replaced by the linear dipole interaction dependence $1/R^3$, resulting from the solution of the secular equation.

The latest achievements of experimental physics in the field of cooling and trapping of atomic gases [1] are widely used to obtain ultracold Rydberg atoms and ultracold plasma [2–6]. The large dipole moment of the Rydberg atoms ($d \approx e n^2 a_0$, $n$—the main quantum number and $a_0$—the Bohr radius) and a large radiative lifetime cause great interest in the study of Rydberg gases. The spatial correlations between Rydberg atoms due to Rydberg blockade effect are the subject of many theoretical and experimental works [7–9]. The energy of this interaction as a function of the distance $R$ between the atoms determines the dependence of the Rydberg blockade radius on the detuning frequency magnitude and the possibility of the existence of ultralong range Rydberg dimers [10].

Van der Waals potential is the second-order approximation of dipole–dipole interaction:

$$V^d = e^2 r_1 r_2 (\sin \vartheta_1 \sin \vartheta_2 \cos (\phi_1 - \phi_2) - 2 \cos \vartheta_1 \cos \vartheta_2) / R^3,$$

where $r_{1,2}$, $\vartheta_{1,2}$, $\phi_{1,2}$—values and angles of radius-vectors in interacting atoms. This approximation is limited by the requirement of its smallness in comparison with the difference between energies of the unperturbed and nearest levels. For the case of two identical atoms in a Rydberg state with principal and orbital numbers $n$ and $l$ the nearest state is one of two-particle states with quantum numbers $n$, $l \pm 1$, so that:

$$\Delta E_{\text{min}} \approx 4Ry\Delta \delta_l/n^3 = 2\Delta \delta_l/n^3 (\text{atomic units}),$$

where $\Delta \delta_l$ equal $\delta_l - \delta_{l+1}$, or $\delta_l - \delta_{l-1}$, or $\delta_l - (\delta_{l+1} + \delta_{l-1})/2$ ($\delta_l$—quantum defect).

Therefore for the value $|V_{\text{vdW}}(R)/\Delta E_{\text{min}}|$, $V_{\text{vdW}}(R) = -C_6/R^6 = -c_6 n^{11}/R^6$, which determines the applicability of van der Waals approximation, we obtain:

$$|V_{\text{vdW}}(R)/\Delta E_{\text{min}}| \approx \left| \frac{c_6 n^{14} 1}{2\Delta \delta_l R^6} \right|.$$
For two atoms \(^{87}\text{Rb}\) in the \(np\) state the closest states is the combination of \(ns\) and \(nd\) atoms (\(|\Delta \delta_p| \approx 0.5\)), and for two atoms \(^7\text{Li}\) in the \(np\) state is the combination of two \(nd\) atoms (\(|\Delta \delta_p| \approx 0.04\)). For two atoms \(^{87}\text{Rb}\) in the \(nd\) state the closest state is the combination of \(np\) and \(nf\) atoms (\(|\Delta \delta_d| \approx 0.08\)), and for \(^7\text{Li}\) it is the combination of two atoms \(nf\) (\(|\Delta \delta_d| \approx 0.002\)).

Introducing LeRoy radius

\[
R_{LR} = 2\sqrt{\frac{r_A^2}{A} + \frac{r_B^2}{B}}
\]

that marks the boundary of applicability of the dipole decomposition, we obtain the condition for the applicability van der Waals approximation in all the region, where the dipole decomposition works:

\[
|V_{vdW}(R_{LR})/\Delta E_{min}| \approx \frac{|c_6|n^{14}}{2\Delta \delta_l^2} \frac{1}{R_{LR}^6} < 1. \quad (3)
\]

Since \(R_{LR} \sim n^2\) and \(c_6 \sim 1/\Delta \delta_l\), and \(|V_{vdW}(R_{LR})/\Delta E_{min}| \sim n^2/\Delta \delta_l^2\), so that for large \(n\) and small \(\Delta \delta_l\) the area of the applicability of van der Waals approximation can be much smaller than the same area of the dipole decomposition.

For the \(np\) state of atoms \(^{87}\text{Rb}\) it may be accepted as a rough estimate \(|c_6| \approx 0.4\) [11] (for different term this variable takes values from 0.2 to 4). Then

\[
|V_{vdW}(R_{LR})/\Delta E_{min}| \approx (n/30)^2.
\]

For atoms \(^7\text{Li}\) in the state of \(nd\) the magnitude \(|c_6|\) can be estimated as \(|c_6| \approx 200\) [11], so that

\[
|V_{vdW}(R_{LR})/\Delta E_{min}| \approx 500n^2.
\]

It means that for these states van der Waals approximation is inapplicable when \(R\) is small even for the minimum value is \(n = 3\). The distance between the particles, where this approximation cannot be used \(R \approx 10(n/100)^{7/3}\).

To determine the electronic terms in the area where van der Waals approximation is not applicable, it is necessary to solve the eigenvalue problem in the space of the two partial states:

\[
\det(E - H^0 - V^d)_{ik} = 0. \quad (4)
\]

The first group of such states includes the states with orbital angular momentum \(l + 1\) and \(l - 1\). There are the states that are associated with the basic state by dipole transition and determine the value \(C_6\). The states of the second group with \(l + 2\) and \(l - 2\) are connected by dipole transition with states of the first group. The following groups formed similarly. For states with the same principal quantum number the total number of such groups is equal to \(n - l - 1\) and the total number of states, including Zeeman sublevels, is of the order \((n - l - 1)^3\).

When solving equation (4) it is necessary to determine that root of the equation which tends to the unperturbed value of the energy \(E_0 = 2E_{nl}\) when \(R \to \infty\) \((V^d \to 0)\).

Matrix \(H^0_{ik}\) is diagonal: \(H^0_{ii} = E_i + \Delta E_i\). The indices \(i\) and \(k\) denote two-particle states \(|n', l', m'|n'', l'', m''\rangle\) and \(\Delta E_i = E_{n'l'} + E_{n''l''} - E_0\). The rank of the matrix in (4) is equal to \(N\)–the number of levels, which is important for determining the interaction energy. The nondiagonal elements of the matrix represent the matrix elements \(V^d \approx 1/R^3\). For large values of \(R\) small \(V^d \approx 1/R^3\) the appropriate solution of equation (4) is \(E = E_0 + V_{vdW}(R)\). For small values of \(R\) the quantities \(\Delta E_i\) can be neglected compared to the matrix elements \(V^d\), as well as to the value \(E - E_0(H^0_{ii} = E_0)\). As a result we have in this case:

\[
\det(E - H^0 - V^d)_{ik} = \sum_{n=1}^{N} \alpha_n (E - E_0)^n R^{-3(N-n)} = R^{-3N} f((E - E_0)R^3). \quad (5)
\]
The interaction energy on \( V \) corresponds to terms of projection of the orbital momentum on the axis passing through the nuclei Λ = 2, which (orthonormal systems of states include one of two basic status of terms)

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It follows from the fact that each term of the determinant consists of \( N \) factors, \( n \) of them are equal to \( E - E_0 \) and the others \( N - n \) are the matrix element of \( V^d \sim 1/R^3 \). Grouping the terms with the same \( n \), we get (5).

Only one of all \( N \) roots of the equation \( f(x) = 0, x = x_0 \), corresponds to that branch of solution, for which \( E(R) \rightarrow E_0 \) when \( R \rightarrow \infty \). For the interaction energy \( V(R) \ (V(R) = E(R) - E_0) \) for small \( R \) we have: \( V(R) = x_0/R^3 \). Thus a quadratic dependence of the dipole interaction energy on \( V_d \ (V(R) \approx 1/R^6) \) at large \( R \) goes to a linear behavior for small \( R \) \( (V(R) \approx 1/R^3) \).

Consider as an example the interaction between two \( ^7\text{Li} \) atoms in the 5d states with total projection of the orbital momentum on the axis passing through the nuclei \( \Lambda = 2, \) which corresponds to terms \( ^1\Delta_u \) and \( ^3\Delta_u \). In this case, it is appropriate to take into account only the states with \( n = 5 \), as these states are the closest in energy to the ground state. The orthonormal systems of states include one of two basic status of terms \( ^1\Delta_u, ^3\Delta_u \) (singlet and triplet states in the area \( R > R_{LR} \) are degenerate):

\[
|\Psi_0^1\rangle = \sqrt{\frac{3}{19}} |5,2,1\rangle |5,2,1\rangle + \sqrt{\frac{8}{19}} |5,2,0\rangle |5,2,2\rangle + |5,2,2\rangle |5,2,0\rangle),
\]

\[
|\Psi_0^2\rangle = \frac{4}{\sqrt{19}} |5,2,1\rangle |5,2,1\rangle - \frac{3}{38} (|5,2,0\rangle |5,2,2\rangle + |5,2,2\rangle |5,2,0\rangle). \tag{6}
\]

States of 1st and 2nd groups for both of these ground states are the same and include six states of the 1st group and nine states of the 2nd group.

In figures 1 and 2 results are presented in the form \( (E - E_0)/\Delta E_{\min} = V(R)/\Delta E_{\min} \) in dependence on \( R/R_{LR} \) in the logarithmic scale \( (\Delta E_{\min} = \text{the minimum energy denominator in the expression for } C_6) \). The results presented in figure 1 correspond to the ground state \( |\Psi_0^1\rangle \) \( (c_6 = 133) \) and figure 2—\( |\Psi_0^2\rangle \) \( (c_6 = 310) \).

These results clearly demonstrate the transition from the asymptotic \( V(R) \sim 1/R^6 \) at large \( R \) to \( V(R) \sim 1/R^3 \) at small \( R \). The figures show that at the left boundary of dipole approximation

\[ \text{Figure 1. Energy of } \Delta \text{ terms for two } ^7\text{Li} \text{ atoms 5d corresponding to the term (6) (}c_6 = 133\). Dashed line—van der Waals potential, solid curve—calculation.} \]

\[ \text{Figure 2. The same as in figure 1 for the state (7). Dashed line—van der Waals potential, solid curve—calculation.} \]
Figure 3. Dashed curve—van der Waals approximation \( (c_6 = 133) \), solid curve—calculation for the term (6), dotted curve—calculation by formula (10).

Figure 4. Dashed curve—van der Waals approximation \( (c_6 = 310) \), solid curve—calculation for the term (7), dotted curve—calculation by formula (10).

Accurate calculation of the electronic term energy with the main quantum number equal to several dozens is very difficult. For approximate calculations it is possible to propose a simple two-level approximation with double-row matrix

\[
\begin{pmatrix}
0 & U(R) \\
U(R) & \Delta E
\end{pmatrix},
\]

with two unknowns \( U(R) \) and \( \Delta E \) (with \( U(R) \to 0 \) at \( R \to \infty \)). The eigenvalue of this matrix we are interesting in is:

\[
V(R) = \frac{\Delta E}{2} (1 - \sqrt{1 + 4U^2(R)/\Delta E^2}).
\]  (8)

For \( R \to \infty \) we have:

\[
V(R) \approx -U^2(R)/\Delta E.
\]

Because in this area \( V(R) \approx V_{vdW}(R) \) it is advisable to define \( U(R) \) by the equation:

\[
U(R) = \sqrt{-V_{vdW}(R)/\Delta E},
\]  (9)

where \( V_{vdW}(R) = -\sum |\alpha_k|^2/\Delta E_k, \Delta E_k = E_k - E_0, \alpha_k = \langle \Psi_0 | V^d(R) | \Psi_k \rangle \). As it follows from the equation (9) \( \Delta E \) must have the sign opposite to the sign of \( V_{vdW}(R) \). The value of \( \Delta E \) can be defined by equality:

\[
\Delta E^{-1} = \langle 1/\Delta E_k \rangle = \sum_k |\alpha_k|^2/\Delta E_k \left( \sum_k |\alpha_k|^2 \right)^{-1}, \quad U(R) = \sqrt{\sum_k |\alpha_k|^2} \sim 1/R^3.
\]

As it follows from the last formulas \( \Delta E \) does not depend on \( R \). Finally, we have:

\[
V(R) = \frac{\Delta E}{2} (1 - \sqrt{1 - 4V_{vdW}(R)/\Delta E}) = \frac{\Delta E}{2} (1 - \sqrt{1 + 4V_{vdW}^2(R)/U^2(R)}).
\]  (10)
For small \( R \), we have
\[ V(R) = -\frac{\Delta E}{|\Delta E|} U(R) = \pm U(R), \]
where the sign coincides with the sign of \( V_{vdW}(R) \). Figures 3 and 4 present the same calculations as in figures 1, 2. Dotted lines are the calculation by formula (10).

Note that two-level approximation does not require any additional information about the dipole transitions above that is used for the calculation of \( C_6 \). This approximation describes the transition from one asymptotic behavior \( (\sim 1/R^6) \) to another one \( (\sim 1/R^3) \) and possibly its point on the distance scale. In the example presented above \( (n = 5) \) this transition takes place in point \( R \approx 200a_0 \). This distance grows as \( n^{7/3} \) so that for selected terms of \( ^7\text{Li} \) transition point is given by formula \( R_n \approx 200(n/5)^{7/3} \) a.u.

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