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Onset of Casimir-Polder retardation in a long-range molecular quantum state

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Abstract

Two ^4He atoms form a diatomic molecule with significant vibrational wave function amplitude at interatomic separations $R > 100 \text{ \AA}$ where the retardation switches the London R^{-6} decay of the potential to the Casimir-Polder (CP) R^{-7} form. It has been assumed that this effect of retardation on the long-range part of the potential is responsible for the 2 \AA (4%) increase of the bond length $\langle R \rangle$ of $^4\text{He}_2$. We show that $\langle R \rangle$ is, unexpectedly, insensitive to the potential at $R > 20 \text{ \AA}$ and its increase is due to quantum electrodynamics effects computed by us from expressions valid at short R —beyond the validity range of CP theory—that seamlessly extend this theory to distances relevant for properties of long molecules.

The perplexing observation made for colloidal systems that the intermolecular potential vanishes with the separation R as R^{-7} rather than as R^{-6} expected from conventional London's theory was explained in 1948 by Casimir and Polder [1] in an early application of quantum electrodynamics (QED) as due to the retardation of electromagnetic interactions at very large R . The so-called Casimir force corresponding to the R^{-7} decay of the potential shows up in only a few physical systems beyond colloids. One of these system was believed to be the single bound state of the $^4\text{He}_2$ molecule, whose very existence was controversial until mid 1990s, but which is now the subject of numerous experiments, see, e.g., Refs. [2–4]. $^4\text{He}_2$ is a model system [5] for similar ultra-long diatomic molecules produced in Bose-Einstein condensates and Fermi gases [6, 7]. The effect of retardation on the size of $^4\text{He}_2$, as measured by the mean interatomic distance $\langle R \rangle$, was computed for the first time by Luo *et al.* [8] in 1993 and found to increase $\langle R \rangle$ by 5.2%. These authors concluded that it is the transition of the interaction potential from the R^{-6} to the R^{-7} dependence, which is essentially completed at distances of the order of 500 Å, and the unusually large long-range tail of the vibrational wave function which make the retardation significantly influence the properties of the bound state of $^4\text{He}_2$. Luo *et al.* also found that the inclusion of the retardation potential at the distances corresponding to the van der Waals minimum (about 3 Å) leads to negligible changes of the properties of $^4\text{He}_2$. According to Spruch [9] “the non-negligible probability of finding [two helium atoms] at $R \sim 100$ Å leads to remarkably large retardation effects of about 10% on the binding energy and about 5% on the mean separation”. This understanding of the phenomenon became generally accepted.

Shortly after the discovery of $^4\text{He}_2$, its size was measured by Luo *et al.* [10], but the experimental uncertainty of 16% was too large to allow conclusions about retardation effects. Later, a more accurate measurement by Grisenti *et al.* [11] gave $\langle R \rangle = 52 \pm 4$ Å, i.e., with a 7.7% error. Several groups performed increasingly accurate calculations of $\langle R \rangle$, with the current best value [12] equal to 47.1 ± 0.5 Å, in fairly good agreement with experiment. Since the neglect of the retardation effect would increase the discrepancy with experiment by about 2 Å, one may claim that such a comparison of theory with experiment represents an observation of the Casimir-Polder retardation in the $^4\text{He}_2$ molecule.

According to Casimir and Polder [1], the retarded interatomic potential is given by

$$V_{\text{CP}}(R) = -\frac{\hbar}{\pi R^6} \int_0^\infty [\alpha_{\text{d}}(i\omega)]^2 e^{-2\omega R/c} P(\omega R/c) d\omega, \quad (1)$$

where $\alpha_d(i\omega)$ is the dipole polarizability of helium atom at the imaginary frequency $i\omega$, c is the speed of light, and $P(x) = x^4 + 2x^3 + 5x^2 + 6x + 3$. At small R , $V_{\text{CP}}(R)$ behaves as $-C_6 R^{-6} + O(\alpha^2)$, where $\alpha = 1/137.036$ is the fine-structure constant and C_6 is the leading van der Waals coefficient in the nonrelativistic Born-Oppenheimer (BO) approximation (we use the convention that this coefficient is positive). Therefore, the appropriate retardation correction to the BO interaction potential $V_{\text{BO}}(R)$ is

$$\delta V_{\text{ret}}^{\text{BO}}(R) = V_{\text{CP}}(R) + C_6 R^{-6}. \quad (2)$$

This retardation correction is equivalent to the replacement of the $-C_6 R^{-6}$ component of the nonrelativistic potential by $-g(R)C_6 R^{-6}$, where $g(R)$ is the *retardation factor* [12, 13]

$$g(R) = -V_{\text{CP}}(R) \frac{R^6}{C_6} \quad (3)$$

[note, that in Ref. [13] the retardation factor of Eq. (3) is denoted by $1 - f(R)$]. The decreasing value of $g(R)$, as it varies from 1 to 0 when R varies from 0 to infinity, corresponds to the increasing importance of the retardation effect. It is the effect of $g(R)$, or equivalently, the addition of $\delta V_{\text{ret}}^{\text{BO}}(R)$ to $V_{\text{BO}}(R)$, which results in the 2.15 Å (or 4.7%) increase of the dimer size [12]. To illustrate the long-range properties of $^4\text{He}_2$, in Fig. 1 we plot the retardation factor $g(R)$ and the vibrational wave function $\chi(R)$. As one can see, the vibrational wave function extends to distances where $g(R)$ differs substantially from unity. For example, at $R = 100$ Å the vibrational wave function amplitude is 34% of its peak value, whereas the value of $g(R)$ is 0.79. Clearly, the retardation effect is already significant between 50 and 250 Å, where the wave function has still a nonegligible amplitude. We found that about 50% of the value of $\langle R \rangle$ comes from $R > 70$ Å and about 10% from $R > 170$ Å.

Figure 1 seems to support the interpretation of Luo *et al.* [8] and Spruch [9]. However, when we attempted to analyze the relations between magnitudes of the adiabatic, relativistic, QED, and retardation contributions to the potential and the corresponding changes of $\langle R \rangle$, we found that a satisfactory correlation could be achieved only when taking into account the region of relatively small R , much below 50 Å. To make sure that indeed there is no sensitivity of the bound state properties to the region where the potential is significantly retarded, we smoothly damped the interaction potential to zero such that the damping is completed between $R = R_d - 1$ Å and $R = R_d + 1$ Å. The dependence of $\langle R \rangle$ and of the dissociation energy D_0 on R_d is shown in Fig. 2. It is seen that the dimer properties do

not depend on $V(R)$ at the distances where the Casimir force is significant. For example, setting $R_d = 20 \text{ \AA}$ gives $\langle R \rangle = 47.19 \text{ \AA}$. This value differs from the exact one by only 0.2%, i.e., much less than the retardation correction computed in Ref. [8]. When $R_d = 30 \text{ \AA}$, this difference reduces to 0.02%. We also found that the asymptotic form of the wave function $\sim e^{-\sqrt{2\mu D_0}R/\hbar}$, where μ is the reduced mass of $^4\text{He}_2$, sets in immediately past the classical outer turning point (equal to 13.6 \AA) and remains practically independent of R_d when $R_d > 20 \text{ \AA}$. This shows that the large amplitudes of the wave function in the classically forbidden region remain practically unchanged if the values of the potential are replaced by zero starting at about 20 \AA . Since the values of the potential for R larger than about 20 \AA are completely irrelevant for the properties of the bound state, the interpretation of Luo *et al.* [8] has to be revised.

One problem with the sensitivity of the bound state to only relatively small values of R is that one may question the validity of $V_{\text{CP}}(R)$ in this region. The CP potential was obtained in the dipole approximation and neglecting charge overlap (penetration) effects. In fact, the issue whether $\delta V_{\text{ret}}^{\text{BO}}(R)$ should be added for all R or only starting from some value where the charge overlap effects can be assumed to be negligible (for example 5 \AA) has been controversial [14]. These questions can be resolved using the relativistic and QED components of the potential computed in Ref. [12]. The total potential from that work is represented as

$$V^{+\text{ret}}(R) = V(R) + \delta V_{\text{ret}}(R), \quad (4)$$

$$V(R) = V_{\text{BO}}(R) + V_{\text{ad}}(R) + V_{\text{rel}}(R) + V_{\text{QED}}(R), \quad (5)$$

where the consecutive terms in Eq. (5) are the BO, adiabatic, α^2 relativistic, and α^3 QED components of the potential computed accurately from formulas valid at any R (without the dipole approximation and with full account of charge overlap effects). The term $\delta V_{\text{ret}}(R)$ in Eq. (4) is the residual retardation correction, defined as the sum of α^n , $n \geq 4$, contributions to $V_{\text{CP}}(R)$.

Let us look more closely at the retardation correction $\delta V_{\text{ret}}^{\text{BO}}(R)$, Eq. (2), at small R . At these distances, $\delta V_{\text{ret}}^{\text{BO}}(R)$ is very well represented by the first two terms of its expansion in powers of α

$$\delta V_{\text{ret}}^{\text{BO}}(R) = -C_4 R^{-4} - C_3 R^{-3} + O(\alpha^4) \quad (6)$$

(the definitions of C_4 and C_3 include the α^2 and α^3 factors, respectively). Although for

very large R (hundreds of angstroms), the correction $\delta V_{\text{ret}}^{\text{BO}}(R)$ is very accurate—bringing about the change from $V_{\text{BO}}(R)$ to $V_{\text{CP}}(R)$ and producing the correct R^{-7} decay of the potential—it is clear that at short range the first two terms of Eq. (6) may represent a poor approximation to the sum of the exact α^2 and α^3 contributions to the potential. A much better approximation at small R is obtained if $-C_4 R^{-4}$ and $-C_3 R^{-3}$ are replaced by the Breit interaction [15] component $V_{\text{Br}}(R)$ of $V_{\text{rel}}(R)$ and by the Araki-Sucher [16, 17] contribution $V_{\text{AS}}(R)$ to $V_{\text{QED}}(R)$, respectively. These contributions to the potential, well defined for all distances (see Ref. [18] for specific expressions and for computational algorithms), result from the exchange of transverse virtual photons and can be viewed as retardation effects. With the replacements mentioned above, one may extend the concept of the retardation correction to smaller R by defining a “short-range” correction of the form

$$\delta V_{\text{sr-ret}}^{\text{BO}}(R) = \delta V_{\text{ret}}^{\text{BO}}(R) + C_4 R^{-4} + C_3 R^{-3} + V_{\text{Br}}(R) + V_{\text{AS}}(R). \quad (7)$$

One can show [19, 20] that $-C_4 R^{-4}$ and $-C_3 R^{-3}$ are the leading terms in the asymptotic, large- R expansion of $V_{\text{Br}}(R)$ and $V_{\text{AS}}(R)$, respectively, so $\delta V_{\text{sr-ret}}^{\text{BO}}(R)$ does not contain any unphysical R^{-4} and R^{-3} long-range contributions to the potential. One can also show that the unphysical long-range R^{-5} contribution to $\delta V_{\text{sr-ret}}^{\text{BO}}(R)$, originating from $V_{\text{AS}}(R)$, can be troublesome, i.e., larger than $V_{\text{CP}}(R)$, only at $R > 0.526/\alpha^2 \text{ \AA} = 0.987 \times 10^4 \text{ \AA}$ [18]. This R^{-5} contribution can be eliminated using the theory developed by Pachucki [20].

We can also relate the retarded potential $V_{\text{BO}}(R) + \delta V_{\text{sr-ret}}^{\text{BO}}(R)$ of Eq. (7) to the $V^{+\text{ret}}(R)$ potential of Eq. (4), the most accurate representation of the interatomic potential available at the present time. The former potential can be also written as

$$V_{\text{BO}}(R) + \delta V_{\text{sr-ret}}^{\text{BO}}(R) = V_{\text{BO}}(R) + V_{\text{Br}}(R) + V_{\text{AS}}(R) + \delta V_{\text{ret}}(R), \quad (8)$$

where

$$\delta V_{\text{ret}}(R) = V_{\text{CP}}(R) + C_6 R^{-6} + C_4 R^{-4} + C_3 R^{-3} \quad (9)$$

is the retardation correction used in Eq. (4). Thus, the additional terms included in $V^{+\text{ret}}(R)$ are $V_{\text{ad}}(R)$ and the relativistic and QED terms other than $V_{\text{Br}}(R)$ and $V_{\text{AS}}(R)$. $V^{+\text{ret}}(R)$ is accurate through α^3 at short and intermediate range. The $\alpha^4 R^{-2}$ contribution included in $\delta V_{\text{ret}}(R)$ may at small R be a poor approximation to the exact α^4 QED correction to the potential, but at such distances the α^4 terms are completely negligible relative to $V_{\text{ad}}(R)$ or $V_{\text{rel}}(R)$.

The terms entering Eq. (7) are shown in Fig. 3. As one can see, $-C_4 R^{-4}$ and $-C_3 R^{-3}$ are very good approximations to $V_{\text{Br}}(R)$ and $V_{\text{AS}}(R)$ even for R as small as the van der Waals minimum distance R_e of 2.96 Å. This resolves the controversy [14] mentioned above in favor of adding $\delta V_{\text{ret}}^{\text{BO}}(R)$ for all R . $V_{\text{Br}}(R) + V_{\text{AS}}(R)$ lies almost everywhere above the corresponding asymptotic approximation, making the potential slightly shallower. This leads to an increase of $\langle R \rangle$ by about 0.3 Å compared to the use of $V_{\text{BO}}(R) + \delta V_{\text{ret}}^{\text{BO}}(R)$.

The BO potential, as well as the leading terms of $\delta V_{\text{sr-ret}}^{\text{BO}}(R)$, are shown in Fig. 4 in the range between 2 and 5 Å. For most of this range, the potential $V_{\text{Br}}(R)$ constitutes only about 0.1% of the magnitude of $V_{\text{BO}}(R)$, and $V_{\text{AS}}(R)$ is still smaller. The only region where $\delta V_{\text{sr-ret}}^{\text{BO}}(R)$ becomes relatively important is around $R = 2.64$ Å, where $V_{\text{BO}}(R)$ crosses zero, but it is too narrow a range of R to have a large influence on the wave function. The relative importance of $\delta V_{\text{sr-ret}}^{\text{BO}}(R)$ increases to about 2.2% as R increases to 20 Å, the upper limit of the sensitive range for the vibrational wave function. Thus, again surprisingly, $\delta V_{\text{sr-ret}}^{\text{BO}}(R)$ in the range 2-20 Å may seem to be too small to account for the 4.7% increase of $\langle R \rangle$. To check this issue, we have multiplied $V_{\text{BO}}(R)$ by 0.999 to make it shallower by the amount of the retardation correction in the region of the potential well. Such a scaled $V_{\text{BO}}(R)$ recovered about two thirds of the retardation effect, showing that small changes in the potential result indeed in disproportionally larger changes in the value of $\langle R \rangle$.

The α^4 retardation correction $\delta V_{\text{ret}}(R)$ of Eq. (9) is negligible up to about 50 Å, but it obviously becomes dominant for much larger distances due to its R^{-3} decay. Although this correction is completely unimportant for the properties of the bound state of $^4\text{He}_2$, it becomes relevant for some thermophysical properties of bulk helium. In particular, the second virial coefficient and the acoustic virial coefficient diverge [18] if the $V(R)$ potential of Eq. (5) is used in quantum scattering calculations (due to its unphysical R^{-3} asymptotics, analogously to the well-known divergence of the S -wave scattering length [21]). Of course, these virials can be calculated without difficulty [18] after adding the retardation correction $\delta V_{\text{ret}}(R)$. In contrast, the viscosity calculations converge with no problems [18] without the $\delta V_{\text{ret}}(R)$ correction.

In conclusion, we have shown that it is indeed the retardation effect that increases the size of the helium dimer bound state by about 5%. However, it is not the retardation in the region of 50-500 Å where the Casimir-Polder effect is significant or dominates, but the retardation effects at the van der Waals minimum and at intermediate distances up to

slightly above the classical outer turning point. These effects, due to the Breit and Araki-Sucher interactions, change the potential by only 0.1% to 2% in this region but lead to much larger changes in the dimer properties.

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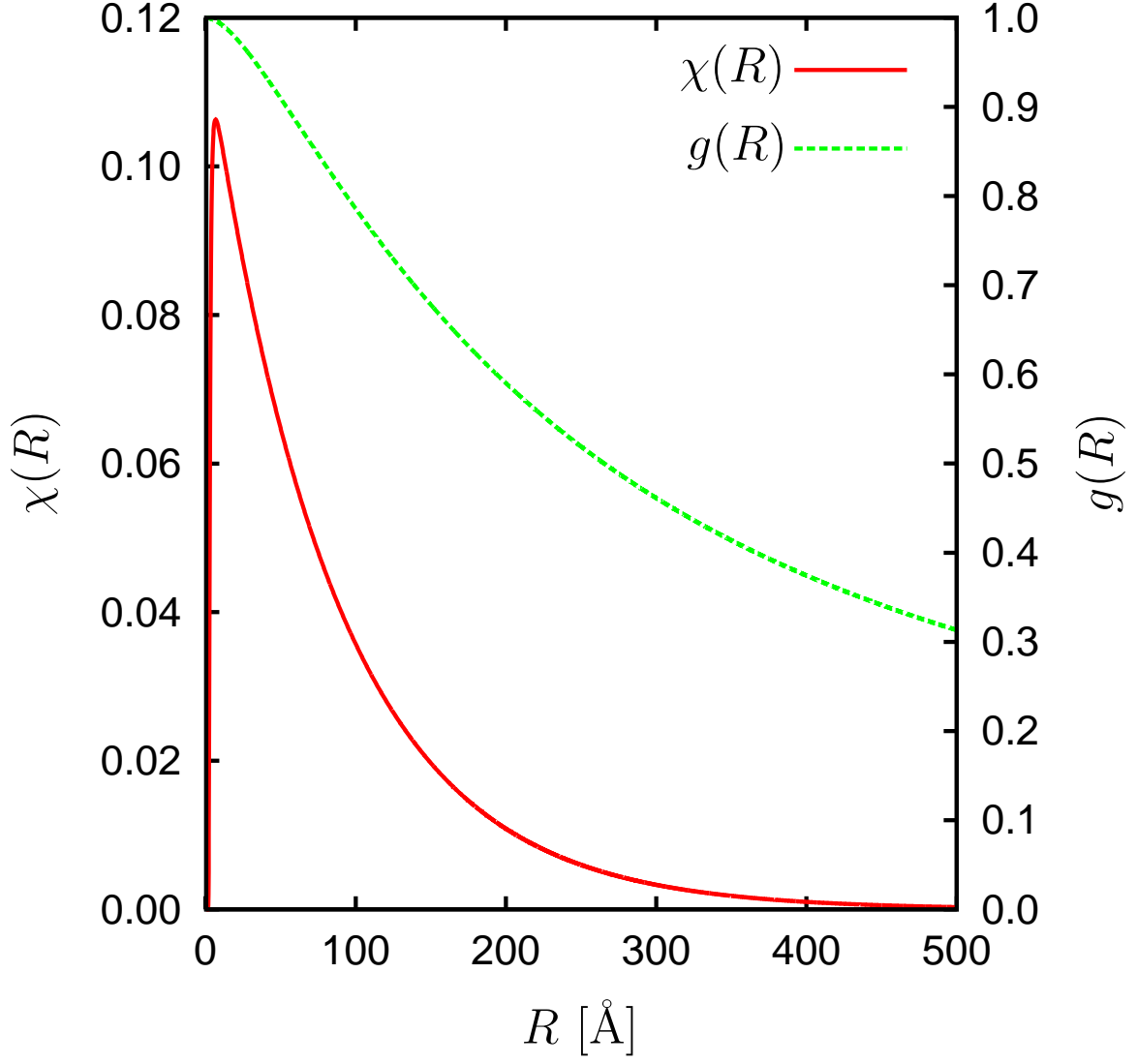


FIG. 1. The vibrational wave function of the helium dimer $\chi(R)$ (left axis), normalized such that $\chi(R)^2$ is the probability density of finding atoms at the distance R , and the retardation factor $g(R)$ showing the increasing importance of the retardation effect at large R (right axis).

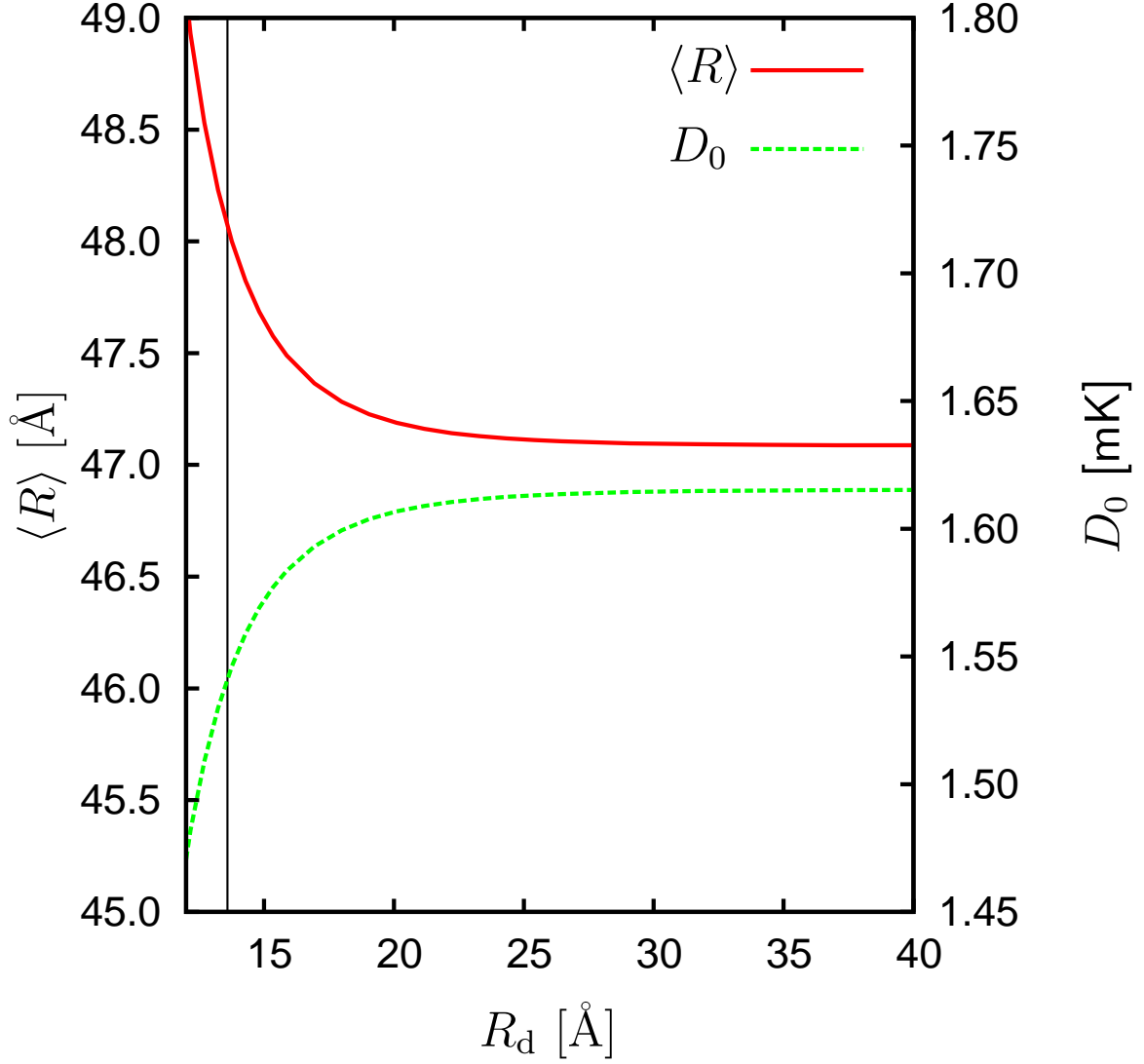


FIG. 2. Dependence of the mean interatomic distance $\langle R \rangle$ in Å (left axis) and of the dissociation energy D_0 in millikelvin (right axis) on the distance R_d where the potential is damped to zero. The vertical line marks the position of the classical outer turning point.

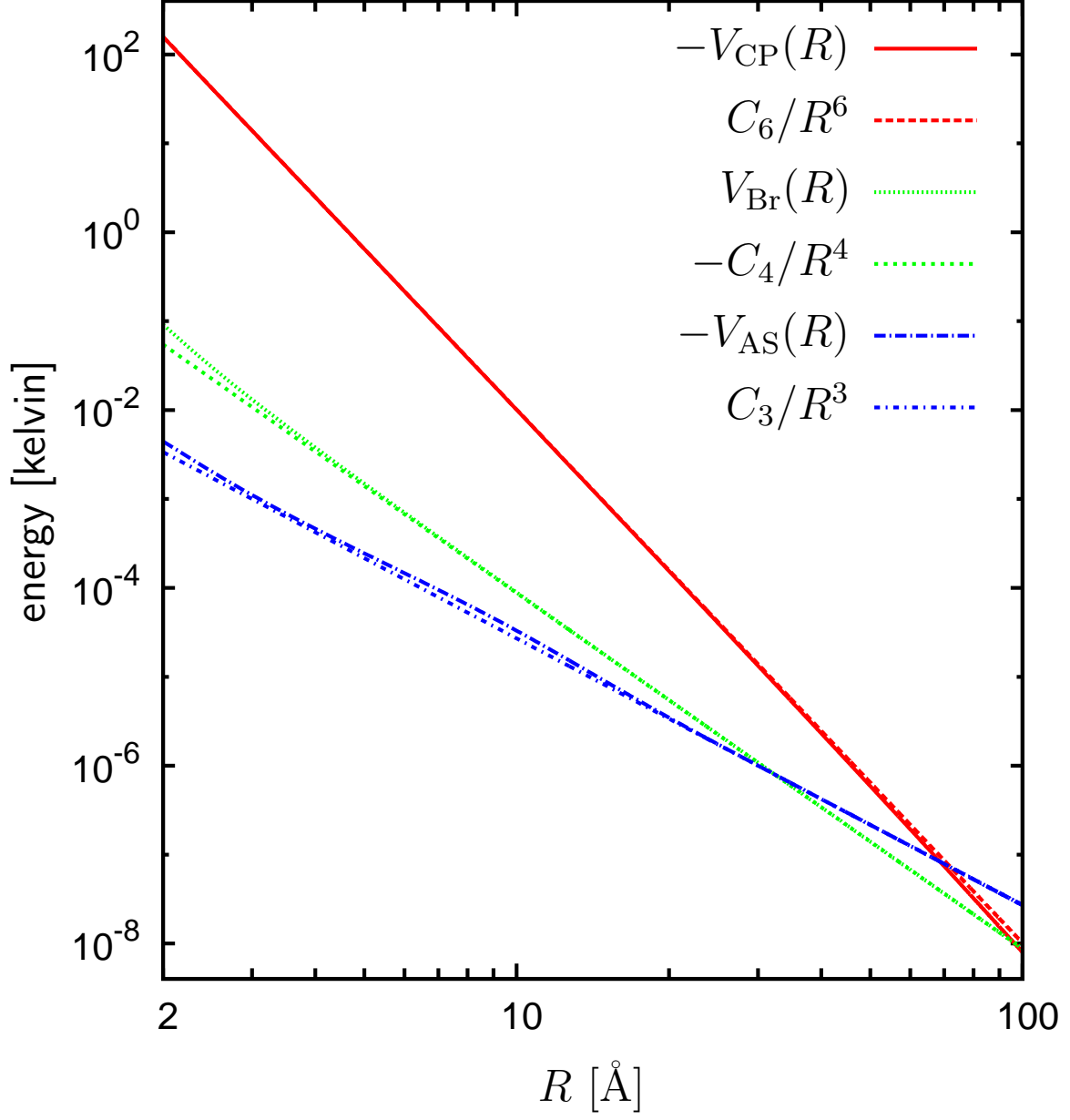


FIG. 3. Comparisons of terms constituting the $\delta V_{\text{sr-ret}}^{\text{BO}}(R)$ retardation correction.

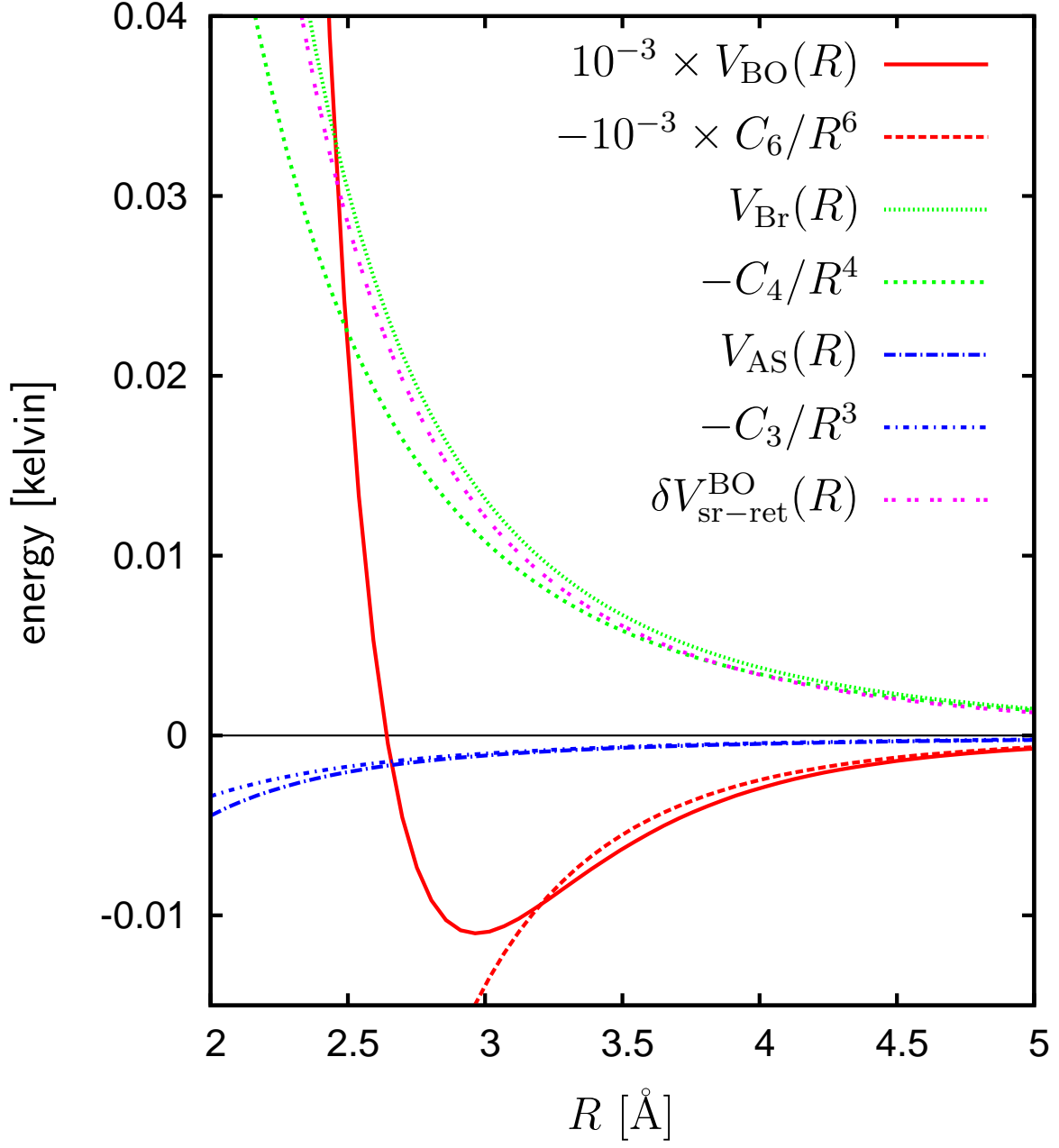


FIG. 4. Comparisons of the components of $\delta V_{\text{sr-ret}}^{\text{BO}}(R)$ with $V_{\text{BO}}(R)$.