Relativistic corrections to the long-range interaction between closed-shell atoms

Krzysztof Pachucki*

Institute of Theoretical Physics, Warsaw University, Hoża 69, 00-681 Warsaw, Poland (Received 31 March 2005; published 14 December 2005)

The complete $O(\alpha^2)$ correction to the long-range interaction between neutral closed-shell atoms is obtained, the relation to the asymptotic expansion of the known short-range interaction at the atomic scale is presented and a general interaction potential that is valid in the whole range of the interatomic distances is constructed.

DOI: 10.1103/PhysRevA.72.062706

PACS number(s): 34.20.Cf, 31.30.Jv

 $E = E(\alpha, mR)$.

The retarded long-range interaction between neutral systems was first considered by Casimir and Polder in their pioneering work in [1]. At large distances atoms interact predominantly by the two-photon exchange with the nonrelativistic dipole interaction $-e\vec{r}\cdot\vec{E}$. There were various extensions of their result. First of all, Feinberg and Sucher in [2] (see also a longer review in [3]) expressed the two-photon exchange interaction (dispersion forces) in terms of the welldefined physical quantities, the invariant amplitudes which describe the elastic scattering of a photon by an atom. These amplitudes are often called dynamic polarizabilities. In this way the authors obtained a formally exact result, as all relativistic corrections are included in the dynamic polarizabilities. In the nonrelativistic limit their result reduces to that of Casimir and Polder. In the limit of large distances their result is expressible in terms of a static electric and magnetic polarizabilities only, similar to the nonrelativistic Casimir-Polder interaction. The calculation of relativistic corrections to the dynamic polarizability is not a simple problem. Therefore, in later works a different approach to dispersion forces was developed that was based on a reformulation of nonrelativistic quantum electrodynamics. Apart from the rederivation of the Casimir-Polder result, there were derived closed formulae for higher multipole interactions such as electric quadrupole [4–6] and electric octupole [7] for isotropic systems, magnetic dipole and diamagnetic couplings for chiral molecules [5]. In this work, using a different reformulation of nonrelativistic quantum electrodynamics [8], we present a systematic derivation of all $O(\alpha^2)$ contributions to the Casimir-Polder potential of closed-shell atoms, including corrections that have not been considered so far. The obtained result is expressible in terms of various corrections to the nonrelativistic dynamic polarizability, in agreement with the general result of Feinberg and Sucher in [2]. Moreover, we present the relation of relativistic corrections to the Casimir-Polder interaction to the short-range nonrelativistic expansion and construct an interaction potential which is valid in the whole range of interatomic distances.

Let us first define the α expansion of the interaction potential in the clamped nuclei approximation. We use natural units, where $c=\hbar=\epsilon_0=1$ and denote by *m* the electron mass. The total energy of a system consisting of two neutral atoms is a function of the fine structure constant α and the distance *R* between these atoms The nonrelativistic expansion in α depends on the magnitude of *R*. According to quantum electrodynamics, if *R* is of the order of an atomic size $R \sim 1/(m\alpha)$, then this expansion at constant $m\alpha R$ takes the form

$$E(\alpha, mR) = E^{(2)}(m\alpha R) + E^{(4)}(m\alpha R) + E^{(5)}(m\alpha R) + O(\alpha^6),$$
(2)

where $E^{(2)}$ is the nonrelativistic energy of order $m\alpha^2$ of a systems of two atoms including Coulomb interactions between all electrons, $E^{(4)}$ is the leading relativistic correction of order $m\alpha^4$, which is given by the Breit-Pauli Hamiltonian δH [9]. We include below only the terms which do not vanish for closed-shell atoms:

$$E^{(4)} = \langle \delta H \rangle, \tag{3}$$

(1)

$$\begin{split} \delta H &= \sum_{a} \left[-\frac{\vec{p}_{a}^{4}}{8m^{3}} + \frac{\pi Z \alpha}{2m^{2}} \delta^{3}(r_{a}) \right] \\ &+ \sum_{a > b} \left[\frac{\pi \alpha}{m^{2}} \delta^{3}(r_{ab}) - \frac{\alpha}{2m^{2}} p_{a}^{i} \left(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^{i} r_{ab}^{j}}{r_{ab}^{3}} \right) p_{b}^{i} \right], \end{split}$$
(4)

where the sum goes over all electrons of both atoms. $E^{(5)}$ is the QED correction of order $m\alpha^5$. It consists of various terms, among others the Araki-Sucher term [10–12], which is dominating at large atomic distances,

$$E^{(5)} = \sum_{a>b} -\frac{14}{3}m\alpha^5 \left\langle \frac{1}{4\pi} P\left(\frac{1}{(m\alpha r_{ab})^3}\right) \right\rangle + \dots$$
(5)

On the other hand, if *R* is of the order of atomic transition wavelength, namely, $R \sim 1/(m\alpha^2)$, then the α expansion at constant $m\alpha^2 R$ takes a completely different form

$$E(\alpha, mR) = E_{\text{free}}(\alpha) + E_{\text{CP}}(m\alpha^2 R) + \delta^{(2)}E_{\text{CP}}(m\alpha^2 R) + \dots,$$
(6)

where E_{free} is the energy of separate atoms, E_{CP} is a Casimir-Polder potential [1] and $\delta^{(2)}E_{\text{CP}}$ is the leading α^2 relativistic correction, which is the subject of this work. The form of this expansion results from the long wavelength formulation of quantum electrodynamics (see Ref. [8]). This relativistic correction to the interaction energy at large atomic distances is obtained from the effective interaction H_I of an atom with the slowly varying electromagnetic field [8]

^{*}Electronic address: krp@fuw.edu.pl; www.fuw.edu.pl/~krp

$$H_{I} = \sum_{a} -e\vec{r}_{a} \cdot \vec{E} - \frac{e}{2} \left(r_{a}^{i} r_{a}^{j} - \frac{\delta^{j}}{3} r_{a}^{2} \right) E_{,j}^{i} - \frac{e}{30} r_{a}^{2} r_{a}^{i} E_{,jj}^{i}$$
$$- \frac{e}{6m} (L_{a}^{i} r_{a}^{j} + r_{a}^{j} L_{a}^{i}) B_{,j}^{i} + \frac{e^{2}}{8m^{2}} (\vec{r}_{a} \times \vec{B})^{2}, \qquad (7)$$

where $\vec{L} = \vec{r} \times \vec{p}$, $\vec{E} = \vec{E}(0)$, $\vec{B} = \vec{B}(0)$ are fields at the position of nucleus, and spin-dependent terms have been neglected as we consider only closed-shell atoms. The sum in Eq. (7) goes over all electrons of one atom. For simplicity, we will assume this sum is present implicitly in all the formulas below. The leading Casimir-Polder interaction comes from the two-photon exchange with the interaction $-e\vec{r}_a \cdot \vec{E}$. Using the temporal gauge for the photon propagator $A^0=0$, it is [13]

$$E_{\rm CP} = -\frac{e^4}{2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} \alpha_{EA}^{ik} \alpha_{EB}^{jl} g^{ij} g^{kl}, \qquad (8)$$

where

$$g^{ij} = \int \frac{d^3k}{(2\pi)^3} e^{i\vec{k}\cdot\vec{R}} \frac{(\omega^2 \vec{\delta}^{ik} - k^i k^k)}{\omega^2 - k^2},$$
 (9)

$$\alpha_E^{ij} = -\left\langle r^i \frac{1}{E - H + \omega} r^j + r^j \frac{1}{E - H - \omega} r^i \right\rangle, \qquad (10)$$

and ω -integration is assumed along the Feynman contour. This integration contour is deformed to imaginary axis by the replacement $\omega = i\lambda$. The *k*-integral leads to

$$g^{ij} = (\lambda^2 \delta^{ij} - \partial^i \partial^j) \frac{e^{-\lambda R}}{R}$$
$$= \frac{e^{-\lambda R}}{R^3} \left[\delta^{ij} (\lambda^2 R^2 + \lambda R + 1) - \frac{R^i R^j}{R^2} (\lambda^2 R^2 + 3\lambda R + 3) \right].$$
(11)

For spherically symmetric states $\alpha_X^{ij} = \delta^{ij} \alpha_X$ and

$$E_{\rm CP} = -\frac{4\alpha^2}{9\pi} \int_0^\infty d\lambda \left\langle \vec{r} \frac{H-E}{(H-E)^2 + \lambda^2} \vec{r} \right\rangle_A \left\langle \vec{r} \frac{H-E}{(H-E)^2 + \lambda^2} \vec{r} \right\rangle_B$$

$$\times \frac{\lambda^4 e^{-2\lambda R}}{R^2} \left(1 + \frac{2}{\lambda R} + \frac{5}{(\lambda R)^2} + \frac{6}{(\lambda R)^3} + \frac{3}{(\lambda R)^4} \right)$$

$$= -\frac{\alpha^2}{\pi} \int_0^\infty d\lambda \; \alpha_{EA}(i\lambda) \alpha_{EB}(i\lambda) \frac{\lambda^4 e^{-2\lambda R}}{R^2}$$

$$\times \left(1 + \frac{2}{\lambda R} + \frac{5}{(\lambda R)^2} + \frac{6}{(\lambda R)^3} + \frac{3}{(\lambda R)^4} \right). \tag{12}$$

This result has been obtained by Casimir and Polder in [1]. We consider here the α^2 correction and represent it as a sum of five terms:

$$\delta^{(2)}E_{\rm CP} = \delta^{(2)}_0 E_{\rm CP} + \delta^{(2)}_1 E_{\rm CP} + \delta^{(2)}_2 E_{\rm CP} + \delta^{(2)}_3 E_{\rm CP} + \delta^{(2)}_4 E_{\rm CP}.$$
(13)

 $\delta_0^{(2)} E_{\text{CP}}$ is due to the Breit-Pauli correction to H, E and state ϕ in Eq. (12). For simplicity we consider corrections only to

the atom A; therefore, only one matrix element in Eq. (12) is to be modified in $\delta_0^{(2)} E_{\rm CP}$, according to

$$\delta_0^{(2)} E_{\rm CP} = -\frac{4\alpha^2}{9\pi} \int_0^\infty d\lambda \, \delta \Biggl\langle \vec{r} \frac{H-E}{(H-E)^2 + \lambda^2} \vec{r} \Biggr\rangle_A \\ \times \Biggl\langle \vec{r} \frac{H-E}{(H-E)^2 + \lambda^2} \vec{r} \Biggr\rangle_B \frac{\lambda^4 e^{-2\lambda R}}{R^2} \Biggl(1 + \frac{2}{\lambda R} + \frac{5}{(\lambda R)^2} \\ + \frac{6}{(\lambda R)^3} + \frac{3}{(\lambda R)^4} \Biggr), \tag{14}$$

$$\delta \left\langle \vec{r} \frac{H-E}{(H-E)^2 + \lambda^2} \vec{r} \right\rangle$$

= $2 \left\langle \delta H \frac{1}{(E-H)'} \vec{r} \frac{H-E}{(H-E)^2 + \lambda^2} \vec{r} \right\rangle$
+ $\frac{1}{2} \left\langle \vec{r} \frac{1}{H-E+i\lambda} (\langle \delta H \rangle - \delta H) \frac{1}{H-E+i\lambda} \vec{r} \right\rangle$
+ $\frac{1}{2} \left\langle \vec{r} \frac{1}{H-E-i\lambda} (\langle \delta H \rangle - \delta H) \frac{1}{H-E-i\lambda} \vec{r} \right\rangle.$ (15)

This correction has recently been considered in Ref. [14]. All remaining corrections to the Casimir-Polder interaction energy are obtained by modification of a dipole interaction $-e\vec{r}\cdot\vec{E}$ by various couplings as given by Eq. (7). $\delta_1^{(2)}E_{\rm CP}$ comes from the quadrupole term $-e/2(r_a^i r_a^j - \delta^{ij} r_a^2/3)E_{ij}^i$ in Eq. (7):

$$\delta_{1}^{(2)}E_{\rm CP} = -\frac{\alpha^2}{120} \int_0^\infty \frac{d\lambda}{2\pi} \left\langle r^{mn} \frac{2(H-E)}{(H-E)^2 + \lambda^2} r^{mn} \right\rangle_A \\ \times \left\langle r^l \frac{2(H-E)}{(H-E)^2 + \lambda^2} r^l \right\rangle_B (\partial^j g^{ik} \partial^j g^{jk} + \partial^p g^{ik} \partial^p g^{ik}),$$
(16)

where

$$r^{ij} \equiv r^i r^j - \frac{\delta^{ij}}{3} r^2. \tag{17}$$

After contracting i, j, k indices, it becomes

$$\delta_{1}^{(2)}E_{\rm CP} = -\frac{\alpha^{2}}{30\pi} \int_{0}^{\infty} d\lambda \left\langle r^{mn} \frac{2(H-E)}{(H-E)^{2} + \lambda^{2}} r^{mn} \right\rangle_{A} \\ \times \left\langle r^{l} \frac{2(H-E)}{(H-E)^{2} + \lambda^{2}} r^{l} \right\rangle_{B} \frac{\lambda^{6}}{R^{2}} e^{-2\lambda R} \left(1 + \frac{6}{\lambda R} + \frac{27}{(\lambda R)^{2}} + \frac{84}{(\lambda R)^{3}} + \frac{162}{(\lambda R)^{4}} + \frac{180}{(\lambda R)^{5}} + \frac{90}{(\lambda R)^{6}} \right).$$
(18)

This result was first obtained by Jenkins, Salam, and Thirunamachandran in [5]. $\delta_2^{(2)}E_{CP}$ is the correction that comes from the term $-e/30r_a^2r_a^iE_{,jj}^i$ in Eq. (7). It is very similar to the dipole-dipole interaction and can easily be obtained on the basis of Eq. (12):

RELATIVISTIC CORRECTIONS TO THE LONG-RANGE ...

$$\delta_{2}^{(2)}E_{\rm CP} = -\frac{4\alpha^{2}}{135\pi} \int_{0}^{\infty} d\lambda \left\langle \vec{r} \frac{H-E}{(H-E)^{2}+\lambda^{2}} r^{2} \vec{r} \right\rangle_{A}$$

$$\times \left\langle \vec{r} \frac{H-E}{(H-E)^{2}+\lambda^{2}} \vec{r} \right\rangle_{B} \frac{\lambda^{6} e^{-2\lambda R}}{R^{2}}$$

$$\times \left(1 + \frac{2}{\lambda R} + \frac{5}{(\lambda R)^{2}} + \frac{6}{(\lambda R)^{3}} + \frac{3}{(\lambda R)^{4}} \right). \quad (19)$$

 $\delta_3^{(2)} E_{\text{CP}}$ is due to $-e/(6m)(L_a^i r_a^j + r_a^j L_a^i)B_j^i$ and can be regarded as another correction to the electric dipole coupling:

$$\delta_{3}^{(2)}E_{\rm CP} = -\frac{4\alpha^{2}}{27\pi} \int_{0}^{\infty} d\lambda \left\langle \vec{r} \frac{1}{(H-E)^{2} + \lambda^{2}} \left(-\frac{i}{2}\right) \right. \\ \left. \times (\vec{L} \times \vec{r} - \vec{r} \times \vec{L}) \right\rangle_{A} \left\langle \vec{r} \frac{H-E}{(H-E)^{2} + \lambda^{2}} \vec{r} \right\rangle_{B} \\ \left. \times \frac{\lambda^{6}e^{-2\lambda R}}{R^{2}} \left(1 + \frac{2}{\lambda R} + \frac{5}{(\lambda R)^{2}} + \frac{6}{(\lambda R)^{3}} + \frac{3}{(\lambda R)^{4}}\right).$$

$$(20)$$

The last correction $\delta_4^{(2)} E_{\rm CP}$ is due to $e^2/(8m^2)(\vec{r}_a \times \vec{B})^2$, and reads

$$\delta_4^{(2)} E_{\rm CP} = -\frac{\alpha^2}{9\pi} \int_0^\infty d\lambda \langle r^2 \rangle_A \left\langle \vec{r} \frac{H-E}{(H-E)^2 + \lambda^2} \vec{r} \right\rangle_B \frac{\lambda^4}{R^2} \times e^{-2\lambda R} \left(1 + \frac{2}{\lambda R} + \frac{1}{(\lambda R)^2} \right). \tag{21}$$

The complete $O(\alpha^2)$ correction is a sum of Eqs. (14) and (18)–(21) as given by Eq. (13). Here, $\delta_1^{(2)}E_{\rm CP}$ comes from interaction between the electric dipole and the electric quadrupole polarizabilities, $\delta_1^{(4)}E_{\rm CP}$ is the interaction energy of the electric dipole polarizability with the magnetic susceptibility, and $E_{\rm CP} + \delta_0^{(2)}E_{\rm CP} + \delta_3^{(2)}E_{\rm CP} + \delta_3^{(2)}E_{\rm CP}$ is the interaction energy between electric dipole polarizabilities α_E with the relativistic correction $\delta^{(2)}\alpha_E$:

$$\alpha_E(i\lambda) \equiv \frac{2}{3} \left\langle \vec{r} \frac{H-E}{(H-E)^2 + \lambda^2} \vec{r} \right\rangle, \tag{22}$$

$$\delta^{(2)}\alpha_{E}(i\lambda) = \frac{2}{3}\delta\left\langle \vec{r}\frac{H-E}{(H-E)^{2}+\lambda^{2}}\vec{r}\right\rangle$$
$$+\frac{2\lambda^{2}}{45}\left\langle \vec{r}\frac{H-E}{(H-E)^{2}+\lambda^{2}}r^{2}\vec{r}\right\rangle$$
$$+\frac{2\lambda^{2}}{9}\left\langle \vec{r}\frac{1}{(H-E)^{2}+\lambda^{2}}\left(-\frac{i}{2}\right)(\vec{L}\times\vec{r}-\vec{r}\times\vec{L})\right\rangle.$$
(23)

We have not found in the literature the complete formula for the leading relativistic correction to the electric dipole polarizability of the closed-shell atoms as that in the Eq. (23).

Let us now consider the large- and small-*R* limits of the interaction energy. At large *R*, the $\delta_0^{(0)} E_{\rm CP}$ and $\delta_4^{(2)} E_{\rm CP}$ contribute to the $1/R^7$ coefficient, but it is only a small correction on the top of $E_{\rm CP}$. Much more interesting is a small-*R*

expansion of $E_{\rm CP}$ and $\delta^{(2)}E_{\rm CP}$ and its relation to the large-*R* expansion of energy as a function of α and $m\alpha R$. This relation has been first considered by Meath and Hirschfelder in [15]. The large-*R* expansion of $E^{(i)}(m\alpha R)$ from Eq. (2) reads

$$E^{(2)} = E_{\text{free}}^{(2)} - m\alpha^2 \left[\frac{C_6^{(2)}}{(m\alpha R)^6} + \frac{C_8^{(2)}}{(m\alpha R)^8} + \dots \right], \quad (24)$$

$$E^{(4)} = E_{\text{free}}^{(4)} - m\alpha^4 \left[\frac{C_4^{(4)}}{(m\alpha R)^4} + \frac{C_6^{(4)}}{(m\alpha R)^6} + \dots \right], \quad (25)$$

$$E^{(5)} = E_{\text{free}}^{(5)} - m\alpha^5 \left[\frac{C_3^{(5)}}{(m\alpha R)^3} + \frac{C_5^{(5)}}{(m\alpha R)^5} + \dots \right], \quad (26)$$

where $C_i^{(j)}$ are dimensionless constants. The relation to the small-*R* expansion of $E_{\rm CP}(m\alpha^2 R)$ and $\delta^{(2)}E_{\rm CP}(m\alpha^2 R)$ from Eq. (6) is the following:

$$E_{\rm CP} = -m\alpha^8 \left[\frac{C_6^{(2)}}{(m\alpha^2 R)^6} + \frac{C_4^{(4)}}{(m\alpha^2 R)^4} + \frac{C_3^{(5)}}{(m\alpha^2 R)^3} + \dots \right],$$
(27)

$$\delta^{(2)}E_{\rm CP} = -m\alpha^{10} \left[\frac{C_8^{(2)}}{(m\alpha^2 R)^8} + \frac{C_6^{(4)}}{(m\alpha^2 R)^6} + \frac{C_5^{(5)}}{(m\alpha^2 R)^5} + \dots \right].$$
(28)

Since both expansions of $E(\alpha, mR)$ involve the same coefficients $C_i^{(i)}$, one can write the general formula

$$E(\alpha, mR) = E_{\text{free}}(\alpha) - \sum_{i,j} m\alpha^{i} \frac{C_{j}^{(i)}}{(m\alpha R)^{j}}.$$
 (29)

We have checked this by equivalence of $C_i^{(j)}$ coefficients as obtained from these two different expansions, and they are equal to (in atomic units)

$$C_{6}^{(2)} = \frac{2}{3} \left\langle r_{A}^{i} r_{B}^{j} \frac{1}{H_{A} + H_{B} - E_{A} - E_{B}} r_{A}^{i} r_{B}^{j} \right\rangle,$$
(30)

$$C_{4}^{(4)} = \frac{2}{9} \left\langle r_{A}^{i} r_{B}^{j} \frac{1}{H_{A} + H_{B} - E_{A} - E_{B}} p_{A}^{i} p_{B}^{j} \right\rangle, \qquad (31)$$

$$C_3^{(5)} = \frac{7}{6\pi} N_A N_B, \tag{32}$$

$$C_{8}^{(2)} = \frac{3}{2} \left\langle \left(r_{A}^{i} r_{A}^{j} - \frac{\delta^{ij}}{3} r_{A}^{2} \right) r_{B}^{k} \frac{1}{H_{A} + H_{B} - E_{A} - E_{B}} \times \left(r_{A}^{i} r_{A}^{j} - \frac{\delta^{ij}}{3} r_{A}^{2} \right) r_{B}^{k} \right\rangle,$$
(33)

,

,

$$C_{6}^{(4)} = \frac{2}{3} \left\langle r_{A}^{i} r_{B}^{j} \frac{1}{H_{A} + H_{B} - E_{A} - E_{B}} (\langle \delta H_{A} \rangle - \delta H_{A}) \right. \\ \left. \times \frac{1}{H_{A} + H_{B} - E_{A} - E_{B}} r_{A}^{i} r_{B}^{j} \right\rangle \\ \left. + \frac{4}{3} \left\langle \delta H_{A} \frac{1}{(E_{A} - H_{A})'} r_{A}^{i} r_{B}^{j} \frac{1}{H_{A} + H_{B} - E_{A} - E_{B}} r_{A}^{i} r_{B}^{j} \right\rangle \\ \left. + \frac{3}{5} \left\langle \left(r_{A}^{i} r_{A}^{j} - \frac{\delta^{i}}{3} r_{A}^{2} \right) r_{B}^{k} \frac{1}{H_{A} + H_{B} - E_{A} - E_{B}} r_{A}^{i} p_{A}^{j} r_{B}^{k} \right\rangle \\ \left. - \frac{2}{15} \left\langle r_{A}^{i} r_{B}^{j} \frac{1}{H_{A} + H_{B} - E_{A} - E_{B}} (2r_{A}^{2} p_{A}^{i} - r_{A}^{i} \vec{r}_{A} \cdot \vec{p}_{A}) r_{B}^{j} \right\rangle,$$

$$(34)$$

$$C_5^{(5)} = \frac{7}{6\pi} \langle r_A^2 \rangle N_B, \qquad (35)$$

where N_A and N_B are the number of electrons in the atoms A and B, respectively. If $\delta^{(2)}E_{\rm CP}$ includes contributions from the atom B, then coefficients $C_6^{(2)}, C_6^{(4)}$, and $C_5^{(5)}$ should include corresponding terms obtained by the replacement $A \leftrightarrow B$.

The $C_j^{(i)}$ coefficients allow one to obtain a convenient form of the interaction potential in the whole region of the atomic distance *R*, as long as these atoms do not overlap. The minimal version of this potential is

$$E = E^{(2)}(m\alpha R) + E_{\rm CP}(m\alpha^2 R) + m\alpha^2 \frac{C_6^{(2)}}{(m\alpha R)^6},$$
 (36)

and the most accurate version using present result is

- [1] H. B. G. Casimir and D. Polder, Phys. Rev. **73** 360 (1948).
- [2] G. Feinberg and J. Sucher, Phys. Rev. A 2, 2395 (1970).
- [3] G. Feinberg, J. Sucher, and C.-K. Au, Phys. Rep. 180, 83 (1989).
- [4] C.-K. Au and G. Feinberg, Phys. Rev. A 6, 2433 (1972).
- [5] J. K. Jenkins, A. Salam, and T. Thirunamachandran, Phys. Rev. A 50, 4767 (1994).
- [6] E. A. Power and T. Thirunamachandran, Phys. Rev. A 53, 1567 (1996).
- [7] A. Salam and T. Thirunamachandran, J. Chem. Phys. 104, 5094 (1996).
- [8] K. Pachucki, Phys. Rev. A 69, 052502 (2004).
- [9] H. A. Bethe and E. E. Salpeter, Quantum Mechanics of

$$E = E^{(2)}(m\alpha R) + E^{(4)}(m\alpha R) + E^{(5)}(m\alpha R) + E_{\rm CP}(m\alpha^2 R) + \delta^{(2)}E_{\rm CP}(m\alpha^2 R) + m\alpha^2 \left[\frac{C_6^{(2)}}{(m\alpha R)^6} + \frac{C_8^{(2)}}{(m\alpha R)^8}\right] + m\alpha^4 \left[\frac{C_4^{(4)}}{(m\alpha R)^4} + \frac{C_6^{(4)}}{(m\alpha R)^6}\right] + m\alpha^5 \left[\frac{C_3^{(5)}}{(m\alpha R)^3} + \frac{C_5^{(5)}}{(m\alpha R)^5}\right].$$
(37)

In summary, the purpose of this work was the derivation of a complete α^2 correction to the Casimir-Polder potential in order to obtain a more accurate description of interatomic interactions in the region where the electron wave functions from different atoms do not overlap. The obtained result can be used for the precise calculation of the scattering length and highly excited vibrational levels of light molecules. Particularly interesting is the helium dimer which existence has been confirmed as recently as 1994 [16]. Its dissociation energy has an extremely small value of 1 mK, while the mean internuclear distance is as large as 50 Å. Its existence can be associated to the long-range attraction between the helium monomers. Since the minor perturbations of the interaction potential result in significant changes in the description of the nuclear motion, the potential in the large range of interatomic distances with an accuracy of the order of 1 mK is needed, which is the magnitude of relativistic and QED effects [17].

ACKNOWLEDGMENTS

I wish to acknowledge interesting discussions with Bogumił Jeziorski and Grzegorz Łach.

One- and Two-Electron Atoms (Plenum, New York, 1977).

- [10] H. Araki, Prog. Theor. Phys. 17, 619 (1957).
- [11] J. Sucher, Phys. Rev. 109, 1010 (1958).
- [12] K. Pachucki, J. Phys. B **31**, 5123 (1998).
- [13] V. B. Berestetsky, E. M. Lifshitz, and L. P. Pitaevsky, *Quantum Electrodynamics* (Pergamon, Oxford, 1982).
- [14] R. Moszynski, G. Łach, M. Jaszuński, and B. Bussery-Honvault, Phys. Rev. A 68, 052706 (2003).
- [15] W. J. Meath and J. O. Hirschfelder. J. Chem. Phys. 44, 3197 (1966); 44, 3210 (1966).
- [16] W. Schöllkopf and J. P. Toennies, Science 266, 1345 (1994).
- [17] W. Cencek, J. Komasa, K. Pachucki, and K. Szalewicz, Phys. Rev. Lett. 95, 233004 (2005).