

Electromagnetic-energy-density distribution around a ground-state hydrogen atom and connection with van der Waals forces

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(Received 28 January 1986)

A spinless hydrogen atom coupled to the electromagnetic field is considered within the context of nonrelativistic quantum electrodynamics. The atom-field interaction is taken in the minimal-coupling form and the Coulomb gauge is used. When the coupled system is in its ground state the electromagnetic field fluctuates away from the vacuum state and the atom has virtual admixtures from its uncoupled lowest eigenstate. The electric- and magnetic-field-energy densities that arise from the fluctuations are determined as functions of the distance from the atom. The relationship between these field-energy densities and the retarded long-range van der Waals forces is also discussed.

I. INTRODUCTION

It is well known that an atom interacting with the electromagnetic vacuum field, in the ground state of the coupled system, is permanently surrounded by a cloud of virtual photons.¹ Recently a detailed study of global and local properties of photon clouds²⁻⁴ and the Maxwell fields⁵⁻⁹ in the neighborhood of atoms and molecules has been made.

The cloud of virtual photons surrounding the atom is related to the retarded van der Waals forces between two polarizable neutral atoms or molecules. In fact, these forces, in addition to the electrostatic interactions, derive from the exchange of transverse virtual photons between the two atoms;^{10,11} it follows that an atom is sensitive to the virtual photon cloud of the other atom.

The aim of this paper is to study the electromagnetic (e.m.) energy density associated with the photon cloud in the Coulomb gauge, and to show the relationship between the virtual fields and the retarded intermolecular forces, a point that was not discussed in the previous papers on the photon clouds,³ where the spatial behavior obtained for the photon cloud was different from the one expected from the theory of intermolecular forces. In this theory it is possible to think of the intermolecular potential as the

result of the interaction of the second atom, seen as a polarizable test body, in the field of the first;^{5,10-12} therefore the intermolecular potential can give information about the characteristics of the virtual fields around the atom. The relevant point is that the field quantity utilized to describe the photon cloud, the coarse-grained energy density operator $W(\mathbf{r})$,³ is different from the square of the total electric field to which, in the intermolecular forces theory, the second atom "responds" in the field of the first. Therefore it is natural that the results of the two cases are different, because the virtual field structure has been described using different quantities having different physical meaning. We show in this paper that on describing the virtual field by the square of the e.m. fields inclusive of the longitudinal part of the field created by the atom, we obtain results directly related to the theory of intermolecular forces. Moreover, we analyze in a detailed way all contributions to the total energy density, stressing the role and the physical meaning of each contribution.

II. ELECTROMAGNETIC FIELD AND ATOM-FIELD INTERACTION

Assuming spherical boundary conditions, the expressions for the transverse e.m. field operators in the Coulomb gauge and in the continuum limit are^{3,13}

$$\begin{aligned}
 \mathbf{A}(\mathbf{r}) = & 2\sqrt{\hbar c} \sum_{l,m} \int_0^\infty \left[j_l(kr) \mathbf{Y}_{lm0}(\theta, \phi) \alpha(k, \mathcal{M}, l, m) \right. \\
 & \left. + \frac{1}{\sqrt{2l+1}} [\sqrt{l} j_{l+1}(kr) \mathbf{Y}_{lm+}(\theta, \phi) - \sqrt{l+1} j_{l-1}(kr) \mathbf{Y}_{lm-}(\theta, \phi)] \alpha(k, \mathcal{E}, l, m) \right] \\
 & \times k^{1/2} dk + \text{H.c.} ,
 \end{aligned}
 \tag{2.1}$$

$$\begin{aligned} \mathbf{E}_\perp(\mathbf{r}) = & i2\sqrt{\hbar c} \sum_{l,m} \int_0^\infty \left\{ j_l(kr) \mathbf{Y}_{lm0}(\theta, \phi) \alpha(k, \mathcal{M}, l, m) \right. \\ & \left. + \frac{1}{\sqrt{2l+1}} [\sqrt{l} j_{l+1}(kr) \mathbf{Y}_{lm+}(\theta, \phi) - \sqrt{l+1} j_{l-1}(kr) \mathbf{Y}_{lm-}(\theta, \phi)] \alpha(k, \mathcal{E}, l, m) \right\} k^{3/2} dk \\ & + \text{H.c.}, \end{aligned} \quad (2.2)$$

$$\begin{aligned} \mathbf{B}(\mathbf{r}) = & -i2\sqrt{\hbar c} \sum_{l,m} \int_0^\infty \left\{ j_l(kr) \mathbf{Y}_{lm0}(\theta, \phi) \alpha(k, \mathcal{E}, l, m) \right. \\ & \left. - \frac{1}{\sqrt{2l+1}} [\sqrt{l} j_{l+1}(kr) \mathbf{Y}_{lm+}(\theta, \phi) - \sqrt{l+1} j_{l-1}(kr) \mathbf{Y}_{lm-}(\theta, \phi)] \alpha(k, \mathcal{M}, l, m) \right\} \\ & \times k^{3/2} dk + \text{H.c.}, \end{aligned} \quad (2.3)$$

where $\lambda = \mathcal{M}, \mathcal{E}$ refers to magnetic and electric multipoles, $j_l(kr)$ are spherical Bessel functions, and \mathbf{Y}_{lmi} are spherical vector harmonics defined as

$$\mathbf{Y}_{lm-} = i^{l+1} \left[\frac{l}{2l+1} \right]^{1/2} \left[\mathbf{P}_{lm} + \left[\frac{l+1}{l} \right]^{1/2} \mathbf{B}_{lm} \right], \quad (2.4)$$

$$\mathbf{Y}_{lm0} = i^l \mathbf{C}_{lm}, \quad (2.5)$$

$$\mathbf{Y}_{lm+} = i^{l-1} \left[\frac{l+1}{2l+1} \right]^{1/2} \left[\mathbf{P}_{lm} - \left[\frac{l}{l+1} \right]^{1/2} \mathbf{B}_{lm} \right]. \quad (2.6)$$

The vector spherical functions \mathbf{P}_{lm} , \mathbf{B}_{lm} , and \mathbf{C}_{lm} are defined as follows:

$$\mathbf{P}_{lm}(\theta, \phi) = \hat{\mathbf{r}} Y_l^m(\theta, \phi), \quad (2.7)$$

$$\mathbf{B}_{lm}(\theta, \phi) = \frac{r}{\sqrt{l(l+1)}} \nabla Y_l^m(\theta, \phi), \quad (2.8)$$

$$\mathbf{C}_{lm}(\theta, \phi) = -\hat{\mathbf{r}} \times \mathbf{B}_{lm}(\theta, \phi), \quad (2.9)$$

where $Y_{lm}(\theta, \phi)$ are the usual spherical harmonics. Equations (2.7), (2.8), and (2.9) are analogous to the vector harmonics of Morse and Feshbach¹³ but differ in the choice of normalization.

The Bose α operators satisfy the following commutation relations:

$$[\alpha(k, \lambda, l, m), \alpha(k', \lambda', l', m')] = 0, \quad (2.10)$$

$$[\alpha(k, \lambda, l, m), \alpha^\dagger(k', \lambda', l', m')] = \delta(k - k') \delta_{\lambda\lambda'} \delta_{ll'} \delta_{mm'}. \quad (2.11)$$

The following properties of the vector spherical harmonics

where

$$\begin{aligned} H_i^1 = & -\frac{e}{mc} \mathbf{A}(\mathbf{r}) \cdot \mathbf{p} = -\frac{2e\hbar^{1/2}}{mc^{1/2}} \sum_{l,m} \int_0^\infty \left\{ j_l(kr) \mathbf{Y}_{lm0} \cdot \mathbf{p} \alpha(k, \mathcal{M}, l, m) \right. \\ & \left. + \frac{1}{\sqrt{2l+1}} [\sqrt{l} j_{l+1}(kr) \mathbf{Y}_{lm+}(\theta, \phi) \cdot \mathbf{p} - \sqrt{l+1} j_{l-1}(kr) \mathbf{Y}_{lm-}(\theta, \phi) \cdot \mathbf{p}] \alpha(k, \mathcal{E}, l, m) \right\} \\ & \times k^{1/2} dk + \text{H.c.}, \end{aligned} \quad (2.18)$$

and, writing down explicitly only terms proportional to $\alpha_k^\dagger \alpha_k^\dagger$, because the others do not contribute to the quantities in

ics defined in the preceding will be often used:

$$\mathbf{Y}_{lmi}^* = (-1)^{l+m+i} \mathbf{Y}_{l-m-i}, \quad (2.12)$$

$$\int d\Omega \mathbf{Y}_{lmi}^* \cdot \mathbf{Y}_{l'm'i'} = \delta_{ll'} \delta_{mm'} \delta_{ii'}, \quad (2.13)$$

$$\sum_m \mathbf{Y}_{lmi}^* \cdot \mathbf{Y}_{lmi'} = \frac{2l+1}{4\pi} \delta_{ii'}, \quad (2.14)$$

where $i=0, +, -$; in the factor $(-1)^{l+m+i}$ in the right-hand side of (2.12) it must be assumed that $i=0, +, -$ corresponding to $i=0, +, -$.

In terms of the field operators (2.2) and (2.3) the field Hamiltonian, subtracting the zero-point energy E_{zp} , is

$$\begin{aligned} H_f = & \frac{1}{8\pi} \int d^3r (\mathbf{E}_\perp^2 + \mathbf{B}^2) - E_{zp} \\ = & \sum_{\lambda, l, m} \int dk \hbar \omega_k \alpha^\dagger(k, \lambda, l, m) \alpha(k, \lambda, l, m). \end{aligned} \quad (2.15)$$

Our physical system is a spinless hydrogen atom interacting with the quantized e.m. field. The atomic part of the Hamiltonian of this system is

$$H_a = \frac{1}{2m} p^2 - \frac{e^2}{r} = \sum_{N, L, M} E_N |\Phi_{NLM}\rangle \langle \Phi_{NLM}|, \quad (2.16)$$

where Φ_{NLM} are eigenstates of the hydrogen atom of energy E_N and quantum numbers N, L, M ; in the sum over N the integration over the continuum states of the atom is also included.

Finally, the interaction Hamiltonian in the minimal-coupling scheme is

$$H_i = H_i^1 + H_i^2, \quad (2.17)$$

which we are interested,

$$\begin{aligned}
H_i^2 &= \frac{e^2}{2mc^2} \mathbf{A}^2(\mathbf{r}) \\
&= \frac{2\hbar e^2}{mc} \sum_{l,m} \int_0^\infty dk \int_0^\infty dk' \left[j_l(kr) \mathbf{Y}_{lm}^* \alpha^\dagger(k, \mathcal{M}, l, m) \right. \\
&\quad \left. + \frac{1}{\sqrt{2l+1}} [\sqrt{l} j_{l+1}(kr) \mathbf{Y}_{lm}^* - \sqrt{l+1} j_{l-1}(kr) \mathbf{Y}_{lm}^*] \alpha^\dagger(k, \mathcal{E}, l, m) \right] \\
&\quad \cdot \left[j_{l'}(k'r) \mathbf{Y}_{l'm'}^* \alpha^\dagger(k', \mathcal{M}, l', m') \right. \\
&\quad \left. + \frac{1}{\sqrt{2l'+1}} [\sqrt{l'} j_{l'+1}(k'r) \mathbf{Y}_{l'm'}^* \right. \\
&\quad \left. - \sqrt{l'+1} j_{l'-1}(k'r) \mathbf{Y}_{l'm'}^*] \alpha^\dagger(k', \mathcal{E}, l', m') \right] (kk')^{1/2} + \dots \quad (2.19)
\end{aligned}$$

We will need the expressions for the longitudinal field created by our system. Let $\mathbf{0}$ be the position of the atomic nucleus, \mathbf{r} the position of the electron, and θ the angle between \mathbf{r} and the observation point \mathbf{R} . Assuming $R \gg r$, the electrostatic potential in \mathbf{R} due to the electron-nucleus system is

$$\begin{aligned}
\Phi(\mathbf{R}) &= -\frac{e}{R} + \frac{e}{|\mathbf{R}-\mathbf{r}|} \\
&= \frac{4\pi e}{R} \sum_{l=1}^{\infty} \frac{(r/R)^l}{2l+1} \sum_{m=-l}^l Y_l^{m*}(\theta_r, \phi_r) Y_l^m(\theta_R, \phi_R). \quad (2.20)
\end{aligned}$$

Therefore, the longitudinal field, that is an operator in the atomic state space, is

$$\begin{aligned}
\mathbf{E}_L(\mathbf{R}) &= -\nabla_{\mathbf{R}} \Phi(\mathbf{R}) \\
&= -4\pi e \sum_{l=1}^{\infty} \frac{r^l}{2l+1} \sum_{m=-l}^l Y_l^{m*}(\theta_r, \phi_r) \\
&\quad \times \nabla_{\mathbf{R}} \left[\frac{1}{R^{l+1}} Y_l^m(\theta_R, \phi_R) \right]. \quad (2.21)
\end{aligned}$$

Using the definitions (2.6), (2.7), and (2.8), we obtain

$$\begin{aligned}
\mathbf{E}_L &= 4\pi e \sum_{l=1}^{\infty} \frac{r^l}{R^{l+2}} (-1)^{-l+1} \left[\frac{l+1}{2l+1} \right]^{1/2} \\
&\quad \times \sum_{m=-l}^l Y_l^{m*}(\theta_r, \phi_r) \mathbf{Y}_{lm+}(\theta_R, \phi_R). \quad (2.22)
\end{aligned}$$

III. GROUND STATE

The unperturbed ground state of our system is $|0\rangle = |\Phi_{100}0\rangle$, where Φ_{100} is the atomic $1s$ ground state and 0 is the photon vacuum; the first-order correction to the unperturbed ground state is³

$$\begin{aligned}
|1\rangle &= \sum_{N,L,M} \int dk (-1)^{M_i-L-1} \frac{\epsilon_{NL}(k)}{\hbar(\omega_{N1} + \omega_k)} \\
&\quad \times |\Phi_{NLM}1(k, \mathcal{E}, L, -M)\rangle, \quad (3.1)
\end{aligned}$$

where the integration over k is intended to extend over all admissible frequencies, $\omega_{N1} = \hbar^{-1} E_{N1} = \hbar^{-1}(E_N - E_1)$ and

$$\begin{aligned}
\epsilon_{NL}(k) &= -\frac{ie\hbar}{ma_0} \left[\frac{\hbar}{\pi c} \right]^{1/2} k^{-1/2} \sqrt{L(L+1)} \\
&\quad \times \langle R_{NL} | j_L(kr) r^{-1} | R_{10} \rangle. \quad (3.2)
\end{aligned}$$

The volume element in the radial matrix elements is $r^2 dr$.

The second-order correction consists of two contributions, one deriving from the second-order treatment of H_i^1 , and the other from the first-order treatment of H_i^2 . Using usual second-order expressions of time-independent perturbation theory,¹⁴ after some calculation we can obtain the contribution $|2\rangle_1$ deriving from H_i^1 ; the part that contributes to the second-order average values in which we are interested is

$$\begin{aligned}
|2\rangle_1 &= \frac{1}{\sqrt{2}\hbar^2} \sum_{N,L,M} \int \int dk dk' (-1)^{M-L} \frac{\epsilon_{NL}(k) \epsilon_{NL}(k')}{\omega_k + \omega_{k'}} \left[\frac{1}{\omega_{N1} + \omega_k} + \frac{1}{\omega_{N1} + \omega_{k'}} \right] \\
&\quad \times |\Phi_{100}1(k, \mathcal{E}, L, M)1(k', \mathcal{E}, L, -M)\rangle. \quad (3.3)
\end{aligned}$$

The contribution due to H_i^2 is

$$|2\rangle_2 = \sum_{L,M} \int \int dk dk' \frac{(-1)^M \eta_L(k, k')}{\hbar(\omega_k + \omega_{k'})} |\Phi_{100} 1(k, \mathcal{M}, L, M) 1(k', \mathcal{M}, L, -M)\rangle \\ + \sum_{L,M} \int \int dk dk' \frac{(-1)^M \xi_L(k, k')}{\hbar(\omega_k + \omega_{k'})} |\Phi_{100} 1(k, \mathcal{E}, L, M) 1(k', \mathcal{E}, L, -M)\rangle, \quad (3.4)$$

where

$$\eta_L(k, k') = -\frac{\sqrt{2}\hbar e^2}{2\pi mc} (-1)^L (kk')^{1/2} \langle R_{10} | j_L(kr) j_L(k'r) | R_{10} \rangle, \quad (3.5)$$

$$\xi_L(k, k') = \frac{\sqrt{2}\hbar e^2}{2\pi mc} (-1)^L (kk')^{1/2} \frac{1}{2L+1} [L \langle R_{10} | j_{L+1}(kr) j_{L+1}(k'r) | R_{10} \rangle \\ + (L+1) \langle R_{10} | j_{L-1}(kr) j_{L-1}(k'r) | R_{10} \rangle]. \quad (3.6)$$

Therefore the relevant part of the ground state up to second-order terms is

$$|\Psi\rangle = N |0\rangle + |1\rangle + |2\rangle_1 + |2\rangle_2, \quad (3.7)$$

where N is a normalization factor.

IV. TOTAL ENERGY DENSITY OF THE VIRTUAL FIELD

Our aim is to calculate the energy density of the electromagnetic field for the perturbed ground state (3.7); this will give us a measure of the virtual photon cloud due to the fluctuations that are associated with the quantum nature of the electromagnetic field.

The energy density of the total electromagnetic field is

$$\mathcal{H}(\mathbf{r}) = \frac{1}{8\pi} [\mathbf{E}^2(\mathbf{r}) + \mathbf{B}^2(\mathbf{r})] \\ = \frac{1}{8\pi} \{[\mathbf{E}_1(\mathbf{r}) + \mathbf{E}_L(\mathbf{r})]^2 + B^2(\mathbf{r})\} \\ = \frac{1}{8\pi} [\mathbf{E}_1^2(\mathbf{r}) + \mathbf{B}^2(\mathbf{r})] + \frac{1}{8\pi} \mathbf{E}_L^2(\mathbf{r}) + \frac{1}{4\pi} \mathbf{E}_1(\mathbf{r}) \cdot \mathbf{E}_L(\mathbf{r}), \quad (4.1)$$

where the subscripts 1 and L refer to transverse and longitudinal parts of the electric field, respectively.

We calculate the transverse part of the energy density (4.1); separating the field operators into their positive and negative frequency parts and after subtraction of the zero-point energy, we have

$$\frac{1}{8\pi} \langle \Psi | \mathbf{E}_1^2 + \mathbf{B}^2 | \Psi \rangle - E_{zp} \\ = \frac{1}{8\pi} \langle \Psi | \mathbf{E}_1^2 + \mathbf{B}^2 | \Psi \rangle - \frac{1}{8\pi} \langle 0 | \mathbf{E}_1^2 + \mathbf{B}^2 | 0 \rangle \\ = \frac{1}{4\pi} \langle 1 | \mathbf{E}_1^- \cdot \mathbf{E}_1^+ + \mathbf{B}^- \cdot \mathbf{B}^+ | 1 \rangle \\ + \frac{1}{4\pi} \text{Re} \{ \langle 0 | \mathbf{E}_1^+ \cdot \mathbf{E}_1^+ + \mathbf{B}^+ \cdot \mathbf{B}^+ | 2 \rangle \}. \quad (4.2)$$

where $|2\rangle = |2\rangle_1 + |2\rangle_2$.

In a previous paper³ we have already calculated the first term in (4.2), that which we called the coarse-grained energy density $W(\mathbf{r})$, and we obtained the following exact result:

$$\frac{1}{4\pi} \langle 1 | \mathbf{E}_1^- \cdot \mathbf{E}_1^+ + \mathbf{B}^- \cdot \mathbf{B}^+ | 1 \rangle \\ = \frac{1}{4\pi} \left[\frac{c}{\pi\hbar} \sum_{N,L} \int \int dk dk' (kk')^{3/2} [L j_{L+1}(kR) j_{L+1}(k'R) + (L+1) j_{L-1}(kR) j_{L-1}(k'R)] \frac{\epsilon_{NL}(k) \epsilon_{NL}^*(k')}{(\omega_{N1} + \omega_k)(\omega_{N1} + \omega_{k'})} \right. \\ \left. + \frac{c}{\pi\hbar} \sum_{N,L} (2L+1) \int \int dk dk' (kk')^{3/2} j_L(kR) j_L(k'R) \frac{\epsilon_{NL}(k) \epsilon_{NL}^*(k')}{(\omega_{N1} + \omega_k)(\omega_{N1} + \omega_{k'})} \right]. \quad (4.3)$$

Using the properties (2.12), (2.13), and (2.14) of the vector spherical harmonics, and making lengthy calculations, we have

$$\begin{aligned}
& \frac{1}{4\pi} \langle 0 | \mathbf{E}_1^+ \cdot \mathbf{E}_1^+ | 2 \rangle \\
&= \frac{1}{4\pi} \left[-\frac{\hbar c}{\pi} \sum_L \int \int dk dk' (kk')^{3/2} (-1)^L \left\{ (2L+1) j_L(kR) j_L(k'R) \frac{\sqrt{2} \eta_L(k, k')}{\hbar(\omega_k + \omega_{k'})} \right. \right. \\
&\quad \left. \left. - [L j_{L+1}(kR) j_{L+1}(k'R) + (L+1) j_{L-1}(kR) j_{L-1}(k'R)] \right. \right. \\
&\quad \left. \left. \times \left[\sum_N \frac{(-1)^L \epsilon_{NL}(k) \epsilon_{NL}(k')}{\hbar^2(\omega_k + \omega_{k'})} \left(\frac{1}{\omega_{N1} + \omega_k} + \frac{1}{\omega_{N1} + \omega_{k'}} \right) \right. \right. \right. \\
&\quad \left. \left. \left. + \frac{\sqrt{2} \xi_L(k, k')}{\hbar(\omega_k + \omega_{k'})} \right] \right] \right] \quad (4.4)
\end{aligned}$$

and

$$\begin{aligned}
& \frac{1}{4\pi} \langle 0 | \mathbf{B}^+ \cdot \mathbf{B}^+ | 2 \rangle \\
&= \frac{1}{4\pi} \left[-\frac{\hbar c}{\pi} \sum_L \int \int dk dk' (kk')^{3/2} (-1)^L \right. \\
&\quad \times \left\{ (2L+1) j_L(kR) j_L(k'R) \left[\sum_N (-1)^L \frac{\epsilon_{NL}(k) \epsilon_{NL}(k')}{\hbar(\omega_k + \omega_{k'})} \left(\frac{1}{\omega_{N1} + \omega_k} + \frac{1}{\omega_{N1} + \omega_{k'}} \right) + \frac{\sqrt{2} \xi_L(k, k')}{\hbar(\omega_k + \omega_{k'})} \right] \right. \\
&\quad \left. \left. + [L j_{L+1}(kR) j_{L+1}(k'R) + (L+1) j_{L-1}(kR) j_{L-1}(k'R)] \frac{\sqrt{2} \eta_L(k, k')}{\hbar(\omega_k + \omega_{k'})} \right] \right\}. \quad (4.5)
\end{aligned}$$

We now consider the terms in the energy density (4.1) that involve the longitudinal electric field. Using (2.22) and (3.7) and retaining the second-order terms only we obtain

$$\frac{1}{8\pi} \langle \Psi | \mathbf{E}_L^2 | \Psi \rangle = \frac{1}{8\pi} \langle 0 | \mathbf{E}_L^2 | 0 \rangle = \frac{1}{8\pi} \left[e^2 \sum_L (L+1) \langle \Phi_{100} | r^{2L} | \Phi_{100} \rangle \frac{1}{R^{2L+4}} \right] \quad (4.6)$$

and

$$\begin{aligned}
\frac{1}{4\pi} \langle \Psi | \mathbf{E}_L \cdot \mathbf{E}_1 | \Psi \rangle &= \frac{1}{2\pi} \text{Re} \{ \langle 0 | \mathbf{E}_L \cdot \mathbf{E}_1 | 1 \rangle \} \\
&= \frac{1}{2\pi} \left[-2ie \left(\frac{\hbar c}{4\pi} \right)^{1/2} \sum_{N,L} \sqrt{L(L+1)} \langle R_{10} | r^L | R_{NL} \rangle \int dk \frac{\epsilon_{NL}(k) k^{3/2}}{\hbar(\omega_{N1} + \omega_k)} j_{L+1}(kR) \frac{1}{R^{L+2}} \right]. \quad (4.7)
\end{aligned}$$

The contributions (4.3)–(4.7) are the exact second-order expectation values for the energy density within our model; however, they are rather complicated and do not show clearly the main features of the virtual fields around the atom. In Sec. V we approximate these expectation values so that the characteristics of these virtual fields are more easily understood.

V. DIPOLE APPROXIMATION

From now on we consider the electric dipole transitions in the atom alone. These dominate all of the higher multipolar and magnetic transitions especially in so far as the fields outside the atom are concerned. Thus we insert $L=1$, $kr \ll 1$ in all radial matrix elements and drop all terms coming from magnetic dipole transitions. So we obtain

$$\epsilon_{N1}(k) \simeq \epsilon_N k^{1/2}; \quad \epsilon_N = -\frac{ie\hbar}{3ma_0} \left(\frac{2\hbar}{\pi c} \right)^{1/2} \langle R_{N1} | R_{10} \rangle, \quad (5.1)$$

$$\xi_1(k, k') \simeq \xi(kk')^{1/2}; \quad \xi = -\frac{\sqrt{2}\hbar e^2}{3\pi mc}, \quad (5.2)$$

$$\eta_1(k, k') \simeq 0. \quad (5.3)$$

Within these approximations, Eqs. (4.3) and (4.4) become

$$\begin{aligned} & \frac{1}{4\pi} \langle 1 | \mathbf{E}_1^- \cdot \mathbf{E}_1^+ + \mathbf{B}^- \cdot \mathbf{B}^+ | 1 \rangle \\ &= \frac{1}{4\pi} \left[\frac{c}{\pi\hbar} \sum_N |\epsilon_N|^2 \int \int dk dk' \frac{(kk')^2}{(\omega_{N1} + \omega_k)(\omega_{N1} + \omega_{k'})} [j_2(kR)j_2(k'R) + 2j_0(kR)j_0(k'R)] \right. \\ & \quad \left. + \frac{3c}{\pi\hbar} \sum_N |\epsilon_N|^2 \int \int dk dk' \frac{(kk')^2}{(\omega_{N1} + \omega_k)(\omega_{N1} + \omega_{k'})} j_1(kR)j_1(k'R) \right], \quad (5.4) \end{aligned}$$

$$\begin{aligned} \frac{1}{4\pi} \langle 0 | \mathbf{E}_1^+ \cdot \mathbf{E}_1^+ | 2 \rangle &= \frac{1}{4\pi} \left\{ \frac{1}{\pi} \int \int dk dk' \frac{(kk')^2}{k+k'} [j_2(kR)j_2(k'R) + 2j_0(kR)j_0(k'R)] \right. \\ & \quad \left. \times \left[\sum_N \frac{|\epsilon_N|^2}{\hbar\omega_{N1}} \left(\frac{\omega_k/\omega_{N1}}{1+\omega_k/\omega_{N1}} + \frac{\omega_{k'}/\omega_{N1}}{1+\omega_{k'}/\omega_{N1}} \right) - \left(2 \sum_N \frac{|\epsilon_N|^2}{\hbar\omega_{N1}} + \sqrt{2}\xi \right) \right] \right\}. \quad (5.5) \end{aligned}$$

Using the Thomas-Reiche-Kuhn sum rule over the atomic levels as given in Appendix A we find that the last term in (5.5) vanishes and we obtain

$$\begin{aligned} \frac{1}{4\pi} \langle 0 | \mathbf{E}_1^+ \cdot \mathbf{E}_1^+ | 2 \rangle &= \frac{1}{4\pi} \left[\frac{1}{\pi} \int \int dk dk' \frac{(kk')^2}{k+k'} [j_2(kR)j_2(k'R) + 2j_0(kR)j_0(k'R)] \right. \\ & \quad \left. \times \sum_N \frac{|\epsilon_N|^2}{\hbar\omega_{N1}} \left(\frac{\omega_k/\omega_{N1}}{1+\omega_k/\omega_{N1}} + \frac{\omega_{k'}/\omega_{N1}}{1+\omega_{k'}/\omega_{N1}} \right) \right]. \quad (5.6) \end{aligned}$$

We can proceed in an analogous way for the magnetic part, Eq. (4.5), obtaining

$$\frac{1}{4\pi} \langle 0 | \mathbf{B}^+ \cdot \mathbf{B}^+ | 2 \rangle = \frac{1}{4\pi} \left[-\frac{3}{\pi} \int \int dk dk' \frac{(kk')^2}{k+k'} j_1(kR)j_1(k'R) \sum_N \frac{|\epsilon_N|^2}{\hbar\omega_{N1}} \left(\frac{1}{1+\omega_k/\omega_{N1}} + \frac{1}{1+\omega_{k'}/\omega_{N1}} \right) \right]. \quad (5.7)$$

Finally, Eqs. (4.6) and (4.7) give

$$\frac{1}{8\pi} \langle \Psi | \mathbf{E}_L^2 | \Psi \rangle = \frac{1}{4\pi} e^2 \langle \Phi_{100} | r^2 | \Phi_{100} \rangle \frac{1}{R^6}, \quad (5.8)$$

$$\frac{1}{4\pi} \langle \Psi | \mathbf{E}_L \cdot \mathbf{E}_1 | \Psi \rangle = \frac{1}{2\pi} (-2e) \left[\frac{\hbar c}{2\pi} \right]^{1/2} \sum_N i\epsilon_N \langle R_{10} | r | R_{N1} \rangle \frac{1}{R^3} \int dk \frac{k^2 j_2(kR)}{\hbar(\omega_{N1} + \omega_k)}. \quad (5.9)$$

We now consider explicitly the behavior of the various terms in the far zone ($R \gg c/\omega_{N1}$) and in the near zone ($a_0 \ll R \ll c/\omega_{N1}$, where a_0 is the Bohr radius).

A. Far zone

If $R \gg c/\omega_{N1}$ we can suppose that in all integrals $\omega_k \ll \omega_{N1}$, and use the following series expansion:

$$\frac{1}{1+x} = 1 - x + x^2 - \dots, \quad (5.10)$$

with $x = \omega_k/\omega_{N1}$.

Using the notation and results of Appendixes A and B, we find that

$$\begin{aligned} \frac{1}{4\pi} \langle 1 | \mathbf{E}_L^- \cdot \mathbf{E}_L^+ | 1 \rangle &= \frac{1}{4\pi} \left[\frac{c}{\pi\hbar} \sum_N \frac{|\epsilon_N|^2}{\omega_{N1}^2} [(\beta_2^2)^2 + 2(\beta_0^2)^2] \frac{1}{R^6} - \frac{c^2}{\pi\hbar} \sum_N \frac{|\epsilon_N|^2}{\omega_{N1}^3} 2(\beta_2^2\beta_1^2 + 2\beta_0^2\beta_1^3) \frac{1}{R^7} + O(R^{-8}) \right] \\ &= \frac{1}{4\pi} \left[\frac{1}{2} e^2 \langle \Phi_{100} | r^2 | \Phi_{100} \rangle \frac{1}{R^6} - \frac{8c\hbar}{\pi} \alpha \frac{1}{R^7} + O(R^{-8}) \right], \end{aligned} \quad (5.11)$$

$$\begin{aligned} \frac{1}{4\pi} \langle 1 | \mathbf{B}^- \cdot \mathbf{B}^+ | 1 \rangle &= \frac{1}{4\pi} \left[\frac{3c}{\pi\hbar} \sum_N \frac{|\epsilon_N|^2}{\omega_{N1}^2} (\beta_1^2)^2 \frac{1}{R^6} - \frac{3c^2}{\pi\hbar} \sum_N \frac{|\epsilon_N|^2}{\omega_{N1}^3} 2\beta_1^2\beta_1^3 \frac{1}{R^7} + O(R^{-8}) \right] \\ &= \frac{1}{4\pi} \left[\frac{8}{3\pi^2} \langle \Phi_{100} | r^2 | \Phi_{100} \rangle \frac{1}{R^6} + O(R^{-8}) \right], \end{aligned} \quad (5.12)$$

$$\begin{aligned} \frac{1}{4\pi} \langle 0 | \mathbf{E}_L^+ \cdot \mathbf{E}_L^+ | 2 \rangle &= \frac{1}{4\pi} \left[\frac{c}{\pi\hbar} \sum_N \frac{|\epsilon_N|^2}{\omega_{N1}^2} [(\beta_2^2)^2 + 2(\beta_0^2)^2] \frac{1}{R^6} - \frac{c^2}{\pi\hbar} \sum_N \frac{|\epsilon_N|^2}{\omega_{N1}^3} (\rho_2 + 2\rho_0) \frac{1}{R^7} + O(R^{-8}) \right] \\ &= \frac{1}{4\pi} \left[\frac{1}{2} e^2 \langle \Phi_{100} | r^2 | \Phi_{100} \rangle \frac{1}{R^6} - \frac{9c\hbar}{4\pi} \alpha \frac{1}{R^7} + O(R^{-8}) \right], \end{aligned} \quad (5.13)$$

$$\begin{aligned} \frac{1}{4\pi} \langle 0 | \mathbf{B}^+ \cdot \mathbf{B}^+ | 2 \rangle &= \frac{1}{4\pi} \left[-\frac{3c}{\pi\hbar} \sum_N \frac{|\epsilon_N|^2}{\omega_{N1}^2} (\beta_1^2)^2 \frac{1}{R^6} + \frac{3c^2}{\pi\hbar} \sum_N \frac{|\epsilon_N|^2}{\omega_{N1}^3} \rho_1 \frac{1}{R^7} + O(R^{-8}) \right] \\ &= \frac{1}{4\pi} \left[-\frac{8}{3\pi^2} e^2 \langle \Phi_{100} | r^2 | \Phi_{100} \rangle \frac{1}{R^6} - \frac{7c\hbar}{4\pi} \alpha \frac{1}{R^7} + O(R^{-8}) \right], \end{aligned} \quad (5.14)$$

and

$$\begin{aligned} \frac{1}{2\pi} \langle 0 | \mathbf{E}_L \cdot \mathbf{E}_L | 1 \rangle &= \frac{1}{2\pi} \left[-\frac{2ie}{\hbar} \left(\frac{\hbar c}{2\pi} \right)^{1/2} \left[\sum_N \frac{1}{\omega_{N1}} \langle R_{10} | r | R_{N1} \rangle \epsilon_N \beta_2^2 \frac{1}{R^6} \right. \right. \\ &\quad \left. \left. - c \sum_N \frac{1}{\omega_{N1}^2} \langle R_{10} | r | R_{N1} \rangle \epsilon_N \beta_2^3 \frac{1}{R^7} + O(R^{-8}) \right] \right] \\ &= \frac{1}{2\pi} \left[-e^2 \langle \Phi_{100} | r^2 | \Phi_{100} \rangle \frac{1}{R^6} + \frac{8c\hbar}{\pi} \alpha \frac{1}{R^7} + O(R^{-8}) \right], \end{aligned} \quad (5.15)$$

where

$$\alpha = \frac{2}{3} \sum_{N,M} \frac{|\langle \Phi_{N1M} | e\mathbf{r} | \Phi_{100} \rangle|^2}{\hbar\omega_{N1}} \quad (5.16)$$

is the static polarizability of the ground state of the hydrogen atom. Equation (5.8) does not need to be approximated.

Finally, collecting all the contributions to the electric and magnetic energy densities we find

$$\frac{1}{8\pi} \langle \Psi | \mathbf{E}^2 | \Psi \rangle - E_{zp} = \frac{1}{8\pi} \left[\frac{23}{2\pi} \hbar c \alpha \frac{1}{R^7} \right] + O(R^{-8}), \quad (5.17)$$

$$\frac{1}{8\pi} \langle \Psi | \mathbf{B}^2 | \Psi \rangle - E_{zp} = \frac{1}{8\pi} \left[-\frac{7}{2\pi} \hbar c \alpha \frac{1}{R^7} \right] + O(R^{-8}). \quad (5.18)$$

B. Near zone

If $R \ll c/\omega_{N1}$ we can suppose $\omega_k \gg \omega_{N1}$ and use (5.10) with $x = \omega_{N1}/\omega_k \ll 1$. In this case the various dominant

contributions to the energy density are, after use of the results of Appendixes A and B,

$$\begin{aligned} \frac{1}{4\pi} \langle 1 | \mathbf{E}_L^- \cdot \mathbf{E}_L^+ | 1 \rangle &= \frac{1}{4\pi} \left[\frac{1}{\pi c \hbar} \sum_N |\epsilon_N|^2 [(\beta_2^1)^2 + 2(\beta_0^1)^2] \frac{1}{R^4} \right], \end{aligned} \quad (5.19)$$

$$\begin{aligned} \frac{1}{4\pi} \langle 1 | \mathbf{B}^- \cdot \mathbf{B}^+ | 1 \rangle &= \frac{1}{4\pi} \left[\frac{3}{\pi c \hbar} \sum_N |\epsilon_N|^2 (\beta_1^1)^2 \frac{1}{R^4} \right], \end{aligned} \quad (5.20)$$

$$\begin{aligned} \frac{1}{4\pi} \langle 0 | \mathbf{E}_L^+ \cdot \mathbf{E}_L^+ | 2 \rangle &= \frac{1}{4\pi} \left[\frac{2}{\pi \hbar} \sum_N \frac{|\epsilon_N|^2}{\omega_{N1}} (\gamma_2^2 + 2\gamma_0^2) \frac{1}{R^5} \right. \\ &\quad \left. - \frac{1}{\pi c \hbar} \sum_N |\epsilon_N|^2 [(\beta_2^1)^2 + 2(\beta_0^1)^2] \frac{1}{R^4} \right], \end{aligned} \quad (5.21)$$

$$\frac{1}{4\pi} \langle 0 | \mathbf{B}^+ \cdot \mathbf{B}^+ | 2 \rangle = \frac{1}{4\pi} \left[-\frac{6}{\pi\hbar} \sum_N \frac{|\epsilon_N|^2}{\omega_{N1}} \gamma_1^2 \frac{1}{R^5} + \frac{3}{\pi c \hbar} \sum_N |\epsilon_N|^2 (\beta_1^1)^2 \frac{1}{R^4} \right], \quad (5.22)$$

$$\frac{1}{2\pi} \langle 0 | \mathbf{E}_L \cdot \mathbf{E}_L | 1 \rangle = \frac{1}{2\pi} \left[-\frac{3}{\hbar} \sum_N \frac{|\epsilon_N|^2}{\omega_{N1}} \beta_2^1 \frac{1}{R^5} \right]. \quad (5.23)$$

If we collect in the electric energy density the terms involving the transverse field, the longitudinal field, and the interference term, the dominant terms are

$$\begin{aligned} \frac{1}{8\pi} \langle \Psi | \mathbf{E}_L^2 | \Psi \rangle - E_{zp} &= \frac{1}{8\pi} \left[\frac{4}{\pi\hbar} (\gamma_2^2 + 2\gamma_0^2) \sum_N \frac{|\epsilon_N|^2}{\omega_{N1}} \frac{1}{R^5} \right] \\ &= \frac{1}{8\pi} \left[\frac{4c}{\pi\hbar} (\gamma_2^2 + 2\gamma_0^2) \sum_N \frac{|\epsilon_N|^2}{\omega_{N1}^2} \left[\frac{\omega_{N1}R}{c} \right] \frac{1}{R^6} \right], \end{aligned} \quad (5.24)$$

$$\begin{aligned} \frac{1}{4\pi} \langle \Psi | \mathbf{E}_L \cdot \mathbf{E}_L | \Psi \rangle &= \frac{1}{4\pi} \left[-\frac{6}{\hbar} \beta_2^1 \sum_N \frac{|\epsilon_N|^2}{\omega_{N1}} \frac{1}{R^5} \right] \\ &= \frac{1}{4\pi} \left[-\frac{6c}{\hbar} \beta_2^1 \sum_N \frac{|\epsilon_N|^2}{\omega_{N1}^2} \left[\frac{\omega_{N1}R}{c} \right] \frac{1}{R^6} \right], \end{aligned} \quad (5.25)$$

$$\begin{aligned} \frac{1}{8\pi} \langle \Psi | \mathbf{E}_L^2 | \Psi \rangle &= \frac{1}{8\pi} \left[2e^2 \langle \Phi_{100} | r^2 | \Phi_{100} \rangle \frac{1}{R^6} \right] \\ &= \frac{1}{8\pi} \left[\frac{9\pi c}{\hbar} \sum_N \frac{|\epsilon_N|^2}{\omega_{N1}^2} \frac{1}{R^6} \right]. \end{aligned} \quad (5.26)$$

We note that, apart from inessential numerical factors, Eqs. (5.24) and (5.25) contain an extra factor $\omega_{N1}R/c$ as compared with (5.26). Since in the near zone this factor is very small the electric energy density in this zone is essentially that arising from the longitudinal part of the electric field

$$\begin{aligned} \frac{1}{8\pi} \langle \Psi | \mathbf{E}^2 | \Psi \rangle - E_{zp} &\simeq \frac{1}{8\pi} \langle \Psi | \mathbf{E}_L^2 | \Psi \rangle \\ &= \frac{1}{8\pi} \left[2e^2 \langle \Phi_{100} | r^2 | \Phi_{100} \rangle \frac{1}{R^6} \right]. \end{aligned} \quad (5.27)$$

With similar arguments we can obtain the dominant term in the magnetic energy density, that is,

$$\begin{aligned} \frac{1}{8\pi} \langle \Psi | \mathbf{B}^2 | \Psi \rangle - E_{zp} &= \frac{1}{8\pi} \left[-\frac{12}{\pi\hbar} \sum_N \frac{|\epsilon_N|^2}{\omega_{N1}} \gamma_1^2 \frac{1}{R^5} \right] \\ &= \frac{1}{8\pi} \left[-\frac{5e^2}{2\pi mc} \frac{1}{R^5} \right]. \end{aligned} \quad (5.28)$$

VI. DISCUSSIONS AND CONCLUSIONS

The results of the previous paragraph allow us to discuss the role of each contribution to the e.m. energy density around the atom. We see that in the asymptotic region the $1/R^6$ behavior of the energy density (5.8) of the longitudinal field is exactly canceled by other $1/R^6$ terms in (5.11), (5.13), and (5.15) due to the transverse field. In other words, one of the effects of retardation in the far zone is to cancel the $1/R^6$ contribution of the static electric dipole. This result, together with the $1/R^7$ behavior of the asymptotic remaining terms in the energy density, is expected from the theory of intermolecular forces where in the far zone retardation effects change the intermolecular potential from $1/R^6$ to $1/R^7$.¹⁰ In fact, if we insert an atom, considered as a test body characterized by a static polarizability α_T^E , in the fluctuating field of the hydrogen atom given by (5.17), the interaction energy is

$$\Delta E_E = -\frac{1}{2} \alpha_T^E \langle \Psi | \mathbf{E}^2(\mathbf{R}) | \Psi \rangle = -\frac{23}{4\pi} \hbar c \alpha \alpha_T^E \frac{1}{R^7}, \quad (6.1)$$

that is, the asymptotic Casimir-Polder potential.^{5,8,10-12}

In the magnetic energy density a cancellation of $1/R^6$ terms between (5.12) and (5.14) occurs in a similar way; it involves the transverse field terms coming from the one- and two-photon states in the perturbed ground state. If the "test" atom also has a magnetic polarizability α_T^M , it interacts with the magnetic part of the fluctuating e.m. fields given by (5.18), and we obtain the following interaction energy:

$$\Delta E_M = -\frac{1}{2} \alpha_T^M \langle \Psi | \mathbf{B}^2(\mathbf{R}) | \Psi \rangle = \frac{7}{4\pi} \hbar c \alpha \alpha_T^M \frac{1}{R^7}, \quad (6.2)$$

as is known.¹¹

Equation (6.1) and (6.2) show that the energy density around the atom, described by the square of the e.m. fields including the longitudinal field, is directly related to the retarded van der Waals forces.

Moreover, the results obtained show that in the near zone the energy density coincides with that due to the longitudinal part of the field alone. This is understandable because in the near zone the retardation corrections contained in the transverse part of the field are negligible; this result agrees with the theory of intermolecular forces where in the near zone it is possible to describe the interaction solely in terms of electrostatic interactions.

We now summarize the results of the work reported in this paper. The fluctuations of the electric and magnetic fields around a nonrelativistic hydrogen atom in its ground state have been studied. These fluctuations have been described by the energy density of the fluctuating e.m. fields. Within second-order perturbation theory, exact expressions for the e.m. energy densities have been obtained, including all multipole transitions. The contribu-

tions from electric dipole transitions are dominant in all region of interest outside the atom and these have been investigated in detail. It has been shown explicitly that there is a cancellation in the far zone between the longitudinal contribution by part of the transverse field contribution. This leaves an energy density with a $1/R^7$ asymptotic behavior. This term involves the transverse field contribution to the energy density and comes from both the one- and two-photon states within the ground state of the coupled system. Moreover, it has been shown that in the near zone all terms involving the transverse field are negligible compared with the pure longitudinal field term. The connection of the fluctuating fields around the atom and the retarded long-range van der Waals forces has also been discussed in the spirit of interpreting the force as the result of the interaction of one atom in the fluctuating field of the other one.

ACKNOWLEDGMENTS

The authors are pleased to thank G. Compagno, F. Persico, and T. Thirunamachandran for many discussions and for collaboration on related problems. They also acknowledge with thanks the receipt of a North Atlantic Treaty Organization research collaborative grant, No. RG85/0112, during which this research was carried out.

APPENDIX A

In this Appendix we give some rules involving the radial matrix elements, which are used in the text of the paper.

The first is an appropriate form of the Thomas-Reiche-Kuhn sum rule

$$\sum_N \frac{1}{E_{N1}} |\langle R_{10} | R_{N1} \rangle|^2 = \frac{3ma_0^2}{2\hbar^2}. \quad (\text{A1})$$

The others are

$$\sum_N \frac{|\epsilon_N|^2}{\omega_{N1}^2} = \frac{2\hbar e^2}{9\pi c} \langle \Phi_{100} | r^2 | \Phi_{100} \rangle, \quad (\text{A2})$$

$$\begin{aligned} \sum_N \frac{|\epsilon_N|^2}{\omega_{N1}^3} &= \frac{2\hbar^2}{9\pi c} \sum_{N,M} \frac{|\langle \Phi_{N1M} | e\mathbf{r} | \Phi_{100} \rangle|^2}{\hbar\omega_{N1}} \\ &= \frac{\hbar^2}{3\pi c} \alpha, \end{aligned} \quad (\text{A3})$$

$$\begin{aligned} \sum_N \frac{1}{\omega_{N1}} \langle R_{10} | r | R_{N1} \rangle \epsilon_N \\ = -\frac{ie}{3} \left[\frac{2\hbar}{\pi c} \right]^{1/2} \langle \Phi_{100} | r^2 | \Phi_{100} \rangle, \end{aligned} \quad (\text{A4})$$

$$\sum_N \frac{1}{\omega_{N1}^2} \langle R_{10} | r | R_{N1} \rangle \epsilon_N = -\frac{i\hbar}{2e} \left[\frac{2\hbar}{\pi c} \right]^{1/2} \alpha, \quad (\text{A5})$$

$$\begin{aligned} \sum_N \langle R_{10} | r | R_{N1} \rangle \langle R_{N1} | R_{10} \rangle \\ = \frac{\hbar}{ma_0} \sum_N \frac{1}{\omega_{N1}} |\langle R_{10} | R_{N1} \rangle|^2 \\ = \frac{3a_0}{2}. \end{aligned} \quad (\text{A6})$$

APPENDIX B

Here we give the following definitions used in the text:

$$\beta_N^M = \lim_{\alpha \rightarrow 0} \int_0^\infty dx e^{-\alpha x} x^M j_N(x), \quad (\text{B1})$$

$$\gamma_N^M = \lim_{\alpha \rightarrow 0} \int_0^\infty dx \int_0^\infty dy \frac{x^M y^M}{x+y} j_N(x) j_N(y) e^{-\alpha(x+y)}, \quad (\text{B2})$$

$$\begin{aligned} \rho_N = \lim_{\alpha \rightarrow 0} \int_0^\infty dx \int_0^\infty dy \frac{x^2 y^2 (x^2 + y^2)}{x+y} \\ \times j_N(x) j_N(y) e^{-\alpha(x+y)} \\ = 2(\beta_N^2 \beta_N^3 - \gamma_N^3), \end{aligned} \quad (\text{B3})$$

where the factor $e^{-\alpha x}$ has been introduced in all integrals to give convergence in the upper limit of integration.

The γ_N^M integrals are calculated explicitly factorizing the x and y integrations by the following relation:

$$\frac{1}{x+y} = \int_0^\infty dt e^{-(x+y)t}. \quad (\text{B4})$$

By extensive use of integral tables¹⁵ we can obtain the particular integrals used in the text of this paper:

$$\begin{aligned} \beta_0^2 = 0; \beta_1^2 = 2; \beta_2^2 = \frac{3\pi}{2}; \beta_0^3 = -2; \beta_1^3 = 0 \\ \beta_2^3 = 8; \rho_2 + 2\rho_0 = \frac{27\pi}{4}; \rho_1 = -\frac{7\pi}{4}; \gamma_1^2 = \frac{5\pi}{8}. \end{aligned} \quad (\text{B5})$$

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