On the Electric-Dipole Representation in Atomic Physics

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I. INTRODUCTION

In non-relativistic quantum mechanics the standard description for an atom interacting with the radiation field is provided by the minimal-coupling (MC) Hamiltonian. As it is well known, the MC Hamiltonian can be obtained in a natural way as a non-relativistic limit for the Dirac Hamiltonian (see e.g. Ref. [1]). Nevertheless it is known also that, in the long-wavelength limit, the gauge coupling of the MC description is replaced usually by the electric-dipole (ED) coupling $-\mathbf{d} \cdot \mathbf{E}$.

The transition from one description to the other one is analysed, in several books, in terms of classical electromagnetic field (see e.g. Ref. [2] [3]). Much more elegant is a method in which, from the beginning, the electromagnetic field is introduced as a quantum field (see e.g. Ref. [4]). Such a procedure is based on the introduction of a unitary transformation, which leads from the MC description to the electric-dipole one is analysed in detail. The momentum cut-off function $\hat{f}_k$ in terms of the electron-density and of the mean-squared value of the electric-dipole moment of the atom in its ground state. A relevant consequence concerns the van der Waals interaction, whose long-distance behaviour turns out to be proportional to $R^{-3}$.

For the sake of simplicity we assume a single electron, we neglect the spin and we assume that the centre-of-mass of the atom be fixed at the position $\mathbf{R}$. In eq.(1.3) the normal ordering, which concerns the $A^2$ term only, has the effect of fixing a reference-level for the energy, according to the following relation

$$\langle g|0|H'_M|g\rangle = \langle g|H_{M0}|g\rangle = E_0.$$  

In eq.(1.4) $|0\rangle$ is the vacuum state for the field,

$$H_{M0} = -\frac{\hbar^2}{2m} \nabla^2 + V(r - \mathbf{R})$$  

is the Hamiltonian for the unperturbed atom and $E_0$ is the energy-eigenvalue corresponding to the ground-state $|g\rangle$.

The transition to the ED representation is accomplished through the following unitary transformation [4]

$$U = \exp\left\{ -\frac{i}{\hbar c} \mathbf{d} \cdot \mathbf{A}(\mathbf{R}) \right\},$$  

where a high-momentum cut-off is understood implicitly.

In this paper we will proceed in the following way. First of all we will introduce a cut-off function $\hat{f}(k)$, for the photon momentum $k$, explicitly in the definition of the unitary transformation $U$ of eq.(1.6). This will be done in eqs (2.1) and (2.3). Subsequently the function $\hat{f}(k)$ will be determined by the variational method. As a result we will obtain for $\hat{f}(k)$ an expression involving the electron-density $\tilde{n}_e(k)$ and the mean-squared value $\langle d^2 \rangle$ of the ED moment of the atom (see eqs.(3.8) in the sequel). In the ED representation the interaction-Hamiltonian will contain the cut-off function $\hat{f}(k)$ explicitly and it will differ significantly from the simple expression $-\mathbf{d} \cdot \mathbf{E}_\perp(\mathbf{R})$, which is used currently.

The case of $N$ atoms is treated in Sec.IV. The unitary transformation is redefined suitably in eq.(4.1). In this case the transformation gives rise to a dipole-dipole interaction among different atoms, to be ascribed to the transverse field. Such an interaction overlaps with the dipole-dipole interaction due to the Coulomb field. As a result, at large distance an exact cancellation of the contributions proportional to $R^{-3}$ occurs. So the leading
contribution to the large-distance dipole-dipole interaction turns out to be proportional to $R^{-4}$. This would imply for the van der Waals potential a leading contribution proportional to $R^{-8}$ and not to $R^{-6}$. This is shown in Sec.V. Actually the experimental status does not look conclusive.

II. THE ELECTRIC-DIPOLE REPRESENTATION

The transition to the ED representation is achieved through the following unitary transformation (Gaussian units are used)

$$U = \exp[-\frac{i}{\hbar c}d \cdot A^f(R)],$$

(2.1)

where

$$d = -e(r - R)$$

(2.2)

is the ED operator. In eq.(2.1) a momentum cut-off has been introduced, by defining

$$A^f(r) = c\sqrt{\frac{2\pi\hbar}{V}} \sum_{k\alpha} \hat{f}(k)\sqrt{\omega_k} e_{k\alpha} a_{k\alpha} e^{ik \cdot r}$$

(2.3)

$$A^f(r) = c\sqrt{\frac{2\pi\hbar}{V}} \sum_{k\alpha} \hat{f}(k)\sqrt{\omega_k} e_{k\alpha} a_{k\alpha} e^{ik \cdot r} + e_{k\alpha}^* a_{k\alpha}^+ e^{-ik \cdot r}.$$ 

In a similar way we define

$$E^f_\perp(r) = i\sqrt{\frac{2\pi\hbar}{V}} \sum_{k\alpha} \hat{f}(k)\sqrt{\omega_k} e_{k\alpha} a_{k\alpha} e^{ik \cdot r}$$

(2.4)

$$E^f_\perp(r) = i\sqrt{\frac{2\pi\hbar}{V}} \sum_{k\alpha} \hat{f}(k)\sqrt{\omega_k} e_{k\alpha} a_{k\alpha} e^{ik \cdot r} - e_{k\alpha}^* a_{k\alpha}^+ e^{-ik \cdot r}.$$ 

The true field operators $A$ and $E_\perp$ correspond to $\hat{f} = 1$.

The real isotropic function $\hat{f}(k)$ carries out the high-momentum cut-off. It will be determined in Sec.III by the variational method.

The presence of the cut-off function $\hat{f}(k)$ affects the commutation relations among field operators, namely

$$[A_i^f(R), E_{\perp j}(r)] = i\hbar c V^{-1} \sum_k e^{ik \cdot (r - R)} \hat{f}(k)(\delta_{ij} - \frac{k_i k_j}{k^2}).$$

(2.5)

Owing to this result, the transverse electric field operator transforms as

$$UE_{\perp j}(r)U^{-1} = E_{\perp j}(r) - \frac{i}{\hbar c} \sum_i d_i [A_i^f(R), E_{\perp j}(r)]$$

(2.6)

$$UE_{\perp j}(r)U^{-1} = E_{\perp j}(r) - \frac{4\pi}{V} \sum_{ki} d_i e^{ik \cdot (r - R)} \hat{f}(k)(\delta_{ij} - \frac{k_i k_j}{k^2}).$$ 

The vector-potential $A_i$, as well as the magnetic-induction $B$, is not modified by the transformation.

These results entail that, in the ED representation, the free-field Hamiltonian $H_F$ reads

$$UH_F U^{-1} = H_F$$

(2.7)

$$- \sum_i d_i V^{-1} \int d r \ E_{\perp j}(r) e^{ik \cdot (r - R)} \hat{f}(k)(\delta_{ij} - \frac{k_i k_j}{k^2})$$

$$+ 2\pi \sum_{ij} d_i d_j V^{-1} \int d k \ f^2(k)(\delta_{ij} - \frac{k_i k_j}{k^2}).$$ 

By calculating the integral in the second term we obtain

$$V^{-1} \sum_{kj} \int d r \ E_{\perp j}(r) e^{ik \cdot (r - R)} \hat{f}(k)(\delta_{ij} - \frac{k_i k_j}{k^2})$$

(2.8)

$$= i\sqrt{\frac{2\pi\hbar}{V}} \sum_{k\alpha} \hat{f}(k)\sqrt{\omega_k} [e_{k\alpha} a_{k\alpha} e^{ik \cdot R} - e_{k\alpha}^* a_{k\alpha}^+ e^{-ik \cdot R}]$$

$$= E^f_{\perp j}(R).$$

The integral in the third term gives

$$2\pi V^{-1} \sum_k \hat{f}^2(k)(\delta_{ij} - \frac{k_i k_j}{k^2})$$

(2.9)

$$\approx \frac{1}{4\pi^2} \int dk \ f^2(k)\left[\frac{2}{3}\delta_{ij} - \frac{k_i k_j}{k^2} - \frac{1}{3}\delta_{ij}\right]$$

$$= \frac{2}{3\pi}\delta_{ij} \int_0^\infty dk \ k^2 f^2(k).$$ 

In performing the calculation, the scalar contribution ($L = 0$) has been separated from the null-trace one ($L = 2$).

In this way we obtain

$$UH_F U^{-1}$$

(2.10)

$$= H_F - d \cdot E^f_\perp(R) + \frac{2}{3\pi} |d|^2 \int_0^\infty dk \ k^2 f^2(k).$$ 

Finally, putting all these results together, we obtain

$$UH_T U^{-1}$$

(2.11)

$$= H_F + \frac{1}{2m} : -i\hbar \nabla + e \frac{c}{\hbar}[A(r) - A^f(R)]^2 :$$

$$+ V(r - R) - d \cdot E^f_\perp(R) + \frac{2}{3\pi} |d|^2 \int_0^\infty dk \ k^2 f^2(k)$$

$$+ \frac{e^2}{2mc^2} (0| A^f(R)|0)$$

$$- \frac{e^2}{2mc^2} (0| A(r) \cdot A^f(R)|0).$$

We have to explicitate the last two terms. From the first one we obtain

$$\frac{e^2}{2mc^2} (0| A^f(R)|0)$$

(2.12)

$$= 2\pi e^2 \lambda_c V^{-1} \sum_k k^{-1} f^2(k) \approx \frac{e^2 \lambda_c}{\pi} \int_0^\infty dk \ k f^2(k),$$ 

$$\frac{e^2}{2mc^2} (0| A(r) \cdot A^f(R)|0).$$
where $\lambda_c = h/mc$ is the Compton wave-length for the electron. From the second term we obtain
\begin{equation}
-\frac{e^2}{mc^2}\langle 0 | A(r) \cdot A'(R) | 0 \rangle \tag{2.13}
= -4\pi e^2\lambda_c V^{-1} \sum_k k^{-1} \hat{f}(k)e^{i\mathbf{k} \cdot (r-R)}
\approx -\frac{e^2\lambda_c}{2\pi^2} \int dk k^{-1} \hat{f}(k)e^{i\mathbf{k} \cdot (r-R)}.
\end{equation}

In this way from eq.(2.11) we obtain
\begin{equation}
UH_TW^{-1} \tag{2.14}
= H_F + \frac{1}{2m} : -i\hbar \nabla + \frac{e}{c} [A(r) - A'(R)]^2 : + V(r-R) - \mathbf{d} \cdot \mathbf{E}_\perp(R) + \frac{2}{3\pi} |\mathbf{d}|^2 \int_0^\infty dk k^2 \hat{f}^2(k)
+ \frac{e^2\lambda_c}{\pi} \int_0^\infty dk k \hat{f}^2(k) - \frac{e^2\lambda_c}{2\pi^2} \int dk k^{-1} \hat{f}(k)e^{i\mathbf{k} \cdot (r-R)}.
\end{equation}

Currently eq.(2.14) is written with $\hat{f} = 1$, and the last two terms (the first of which would diverge for $\hat{f} = 1$, while the second one would give the result $-2e^2\lambda_c \pi^{-1} |r-R|^2$) are neglected. In the $|\mathbf{d}|^2$ term, which diverges also for $\hat{f} = 1$, a momentum cut-off is understood. Nevertheless eq.(2.14) differs from the expression
\begin{equation}
UH_TW^{-1} = H_F + H_M0 - \mathbf{d} \cdot \mathbf{E}_\perp(R), \tag{2.15}
\end{equation}
which is assumed usually.

In the sequel we will refer to eq.(2.14), where the function $\hat{f}$ will be determined in Sec.III by the variational method.

Let us proceed to a preliminary analysis of eq.(2.14). By averaging both sides of eq.(2.14) over the vacuum state of the field we obtain
\begin{equation}
H'M0 \equiv \langle 0 | UH_TW^{-1} | 0 \rangle \tag{2.16}
= H_M0 + \frac{e^2\lambda_c}{\pi} \int_0^\infty dk k \hat{f}^2(k)
+ \frac{2}{3\pi} |\mathbf{d}|^2 \int_0^\infty dk k^2 \hat{f}^2(k)
- \frac{e^2\lambda_c}{2\pi^2} \int dk k^{-1} \hat{f}(k)e^{i\mathbf{k} \cdot (r-R)}.
\end{equation}

This equation can be generalised easily to the case of a many-electron atom.

The hydrogen-atom case is simple. In fact in such a case eq.(2.16) reads
\begin{equation}
H'M0 = H_M0 + V'(r-R), \tag{2.17}
\end{equation}
where the additional potential $V'$ has the form
\begin{equation}
V' = C_0 + \frac{1}{2} n\Omega_0^2 |r-R|^2 + V''(|r-R|). \tag{2.18}
\end{equation}

In eq.(2.18) $C_0$ is the following constant
\begin{equation}
C_0 = \pi^{-1} e^2\lambda_c \int_0^\infty dk k \hat{f}^2(k), \tag{2.19}
\end{equation}
while, for the harmonic-oscillator potential in the second term, one has
\begin{equation}
\frac{1}{2} n\Omega_0^2 = \frac{2e^2}{3\pi} \int_0^\infty dk k^2 \hat{f}^2(k). \tag{2.20}
\end{equation}

Finally the last term consists of the following additional potential
\begin{equation}
V''(r) = -\frac{e^2\lambda_c}{2\pi} \int dk k^{-1} \hat{f}(k)e^{i\mathbf{k} \cdot r} \tag{2.21}
= -\frac{2e^2}{\pi r} \int_0^\infty dk \hat{f}(k) \sin kr \sim \frac{2e^2\lambda_c}{\pi r^2},
\end{equation}
where the last side represents the asymptotic expression for large $r$. In the calculation of the last expression the result $\hat{f}(0) = 1$ has been used. This result will be obtained in the sequel (see eq.(3.9)). We observe that $V''(r)$ does not vanish for $r = 0$. In fact it is
\begin{equation}
V''(0) = -2\pi^{-1} e^2\lambda_c \int_0^\infty dk k \hat{f}(k). \tag{2.22}
\end{equation}

In the case of a $Z$-electron atom, eq.(2.2) is replaced by
\begin{equation}
\mathbf{d} = -e \sum_{A=1}^Z (r_A - R) \tag{2.23}
\end{equation}
and eq.(2.14) reads
\begin{equation}
UH_TW^{-1} \tag{2.24}
= H_F + \frac{1}{2m} \sum_A : -i\hbar \nabla_A + \frac{e}{c} [A(r_A) - A'(R)]^2 : + V^{(1)}(r_A-R) + \sum_{A<B} V^{(2)}(r_A-R_B)
- \mathbf{d} \cdot \mathbf{E}_\perp(R) + \frac{2}{3\pi} |\mathbf{d}|^2 \int_0^\infty dk k^2 \hat{f}^2(k)
+ \pi^{-1} e^2\lambda_c Z \int_0^\infty dk k \hat{f}^2(k)
- \frac{e^2\lambda_c}{2\pi^2} \sum_A \int dk k^{-1} \hat{f}(k)e^{i\mathbf{k} \cdot (r_A-R)}.
\end{equation}

III. VARIATIONAL CALCULATION

We will determine the function $\hat{f}$ by the variational method, assuming a trial state of the form
\begin{equation}
|\psi_T\rangle = U|0\rangle |g\rangle, \tag{3.1}
\end{equation}
where $|g\rangle$ is the ground-state for the unperturbed atom. The corresponding wave-function will be indicated as
\begin{equation}
\phi_0(r - R) = |r|g\rangle. \tag{3.2}
\end{equation}
We observe that the trial state of eq.(3.1) is normalized. For the sake of simplicity we assume that the wave-function $\phi_0$ is isotropic ($l = 0$) and we neglect the spin.

The energy of the system, averaged over the state (3.1),
\begin{equation}
\mathcal{E}_0[\hat{f}] = \langle \psi_T | H_T | \psi_T \rangle = \langle g | 0 \rangle U^{-1} H_T U | 0 \rangle |g\rangle, \tag{3.3}
\end{equation}
depends on $\hat{f}$ functionally. Using eq.(2.16) we can write
\begin{equation}
\mathcal{E}_0[\hat{f}] = E_0 + \pi^{-1} e^2 \lambda_\epsilon \int_0^\infty dk \frac{k \hat{f}^2(k)}{6} \tag{3.4}
\end{equation}
where $E_0$ is the energy of the ground state.

In eq.(3.3) $\langle d^2 \rangle$ is given by
\begin{equation}
\langle d^2 \rangle = e^2 \int d^3 r \frac{r^2 |\phi_0(r)|^2}{(2\pi)^3} \tag{3.5}
\end{equation}
while
\begin{equation}
\hat{n}_e(k) = \int d^3 r e^{ik \cdot r} |\phi_0(r)|^2 \tag{3.6}
\end{equation}
consists of the Fourier-transform of the electron-density $n_e(r) = |\phi_0(r)|^2$. The last side represents the asymptotic behavior for $k \to 0$.

Eq.(3.4) confirms the need for a high-momentum cut-off. In fact it can be seen immediately that for $\hat{f} = 1$ the energy $\mathcal{E}_0$ diverges.

The function $\hat{f}(k)$ can be obtained by minimising the energy $\mathcal{E}_0$ of eq.(3.4). We observe that a vanishing $\hat{f}$ would return the result $\mathcal{E}_0 = E_0$, in agreement with eq.(1.4). Therefore it can be expected that any non-trivial solution $\hat{f}$ to the variational problem would correspond to an energy $\mathcal{E}_0 < E_0$.

By minimising the energy $\mathcal{E}_0[\hat{f}]$ of eq.(3.4) with respect to $\hat{f}(k)$ we obtain the equation
\begin{equation}
0 = \delta \mathcal{E}_0[\hat{f}] / \delta \hat{f}(k) \tag{3.7}
\end{equation}
and a corresponding expression for $a_{\alpha}^+$. In this way we obtain
\begin{equation}
\hat{f}(k) = n_e(k)(1 + n_e(k))^2. \tag{3.8}
\end{equation}

It can be seen immediately that $\hat{f}(0) = 1$, as it could be expected. Furthermore the following asymptotic behaviour for small $k$
\begin{equation}
\hat{f}(k) \sim 1 - \frac{2\langle d^2 \rangle}{3e^2\lambda_\epsilon} k + \ldots \tag{3.9}
\end{equation}
can be derived immediately from eq.s (3.6) and (3.8). Moreover from eq.s (3.8) and (3.6) it follows that, for $k \to \infty$, $\hat{f}(k)$ vanishes as $k^{-3}$.

Finally, using the result of eq.(3.8) in eq.(3.4), we obtain for the energy $\mathcal{E}_0$ the result
\begin{equation}
\mathcal{E}_0[\hat{f}] = E_0 - \pi^{-1} e^2 \lambda_\epsilon \int_0^\infty dk k \hat{f}(k) \hat{n}_e(k) \tag{3.10}
\end{equation}
with $\hat{f}$ given by eq.(3.8). Eq.(3.10) shows that $\mathcal{E}_0[\hat{f}] < E_0$, as expected.

We observe that the second (negative) contribution in eq.(3.10) would have the effect of shifting every energy-level of the atom by the same amount. Therefore such an effect cannot be observed through any spectral-line analysis.

As an example, for the hydrogen atom in the 1s state we have
\begin{equation}
\phi_0(r) = (\pi a^3)^{-1} e^{-r/a}, \tag{3.11}
\end{equation}
and correspondingly
\begin{equation}
e^{-2} \langle d^2 \rangle = 3a^2, \tag{3.12}
\end{equation}
where $a = \hbar^2/2m$ is the Bohr radius. Putting $z_k = 1/2ka$, we have
\begin{equation}
n_e(k) = (1 + z_k^2)^{-2} \sim 1 - \frac{1}{2} k^2 a^2 + \ldots \tag{3.13}
\end{equation}
In this case from eq.(3.8) we obtain
\begin{equation}
\hat{f}(k) = (1 + z_k^2)^{-2}(1 + 4a^{-1} z_k)^{-1} \tag{3.14}
\end{equation}
and a similar expression for $a_{\alpha}^+$. In this way we obtain
\begin{equation}
n_k^{ph} = \sum_{\alpha} \langle g | 0 | U a_{\alpha}^+ a_{\alpha} U^{-1} | 0 \rangle |g\rangle \tag{3.16}
\end{equation}
and
\begin{equation}
n_k^{ph} = \frac{V}{8\pi} \int d\Omega_k k^2 n_k^{ph} = \frac{d^2}{3\pi \hbar c} \hat{f}^2(k) \tag{3.17}
\end{equation}
with a total number of photons given by
\begin{equation}
N_{ph} = \int_0^\infty dk n_k^{ph} = \frac{d^2}{3\pi \hbar c} \int_0^\infty dk k \hat{f}^2(k). \tag{3.18}
\end{equation}
For a hydrogen atom eq.(4.12) gives the result
\[ N_{ph} = \frac{\alpha^3}{4\pi} \int_0^\infty dz \frac{z}{(1+z^2)(z+\alpha/4)^2} \]
\[ \simeq 1.4 \times 10^{-7}. \] (3.19)
For the calculation of the integral see the Appendix A.

It is interesting to note that the maximum value for \( n_{ph} \) is attained for \( z = z_0 = 1/7 \), e.g. for \( \lambda \sim 22a \) in the far-ultraviolet region.

The transformation \( U \) of eq.(2.1) could be introduced in the free-electron case also, in order to seek for a possible spontaneous localisation for the wave-packet, due to the second term in eq.(3.10). For e.g. a Gaussian \( \phi_0 \sim e^{-r^2/a^2} \), eq.(3.10) would give \( \Delta E_0 \sim -\frac{\pi^2}{a} \). But for a non-relativistic electron this negative contribution to the total energy would be too small to have any observable effect.

\[ \text{IV. N ATOMS} \]

In the case of \( N \) identical atoms, the unitary transformation \( U \) of eq.(2.1) becomes
\[ U = \exp[-\frac{i}{\hbar c} \sum_{a=1}^{N} d_a \cdot A^f(R_a)]. \] (4.1)
As a consequence, eq.(2.6) now reads
\[ [UE_{\perp}U^{-1}](r) = E_{\perp}(r) \]
\[ -\frac{4\pi}{V} \sum_a \sum_j \sum_k e^{ik(r-R_a)} \bar{f}(k)(\delta_{ij} - \frac{k_i k_j}{k^2})d_{aj}. \] (4.2)
The Hamiltonian \( H_M \) of eq.(1.3) is replaced by
\[ H_M = \sum_a \frac{1}{2m} : -i\hbar \nabla_a + \frac{e}{c} A(r_a) : \]
\[ +V(r-R_a) + \sum_{a<b} \sum_{ij} g_{ij}(R^{eb}) d_{ij}. \] (4.3)
In eq.(4.3) we have put \( R^{eb} = R_a - R_b \). Furthermore the matrix \( g \) is given by the expression
\[ g_{ij}(R) = R^{-3}(\delta_{ij} - \frac{3X_i X_j}{R^2}) \]
\[ \simeq \frac{4\pi}{V} \sum_k e^{ikR} (\delta_{ij} - \frac{k_i k_j}{k^2}). \] (4.4)
The last expression is correct for \( R > 0 \).

In eq.(4.3) the last term represents an interaction, due to the Coulomb field (longitudinal electric field), among the ED moments belonging to different atoms. In the standard treatment, this term alone is responsible for the van der Waals interaction. In second-order perturbation theory it gives rise to an interaction-potential, whose leading contribution at large distance is proportional to \( R^{-6} \). However we will show that the unitary transformation of eq.(5.1) gives rise to a similar interaction term, to be ascribed to the transverse field. In fact we have
\[ U H_T U^{-1} = H_T \]
\[ + \sum_a \left\{ \frac{1}{2m} : -i\hbar \nabla_a + \frac{e}{c} [A(r_a) - A^f(R_a)] : \right\}^2 : \]
\[ + V(r_a - R_a) - d_a \cdot E^f(R_a) + \frac{2}{3\pi} |da|^2 \int_0^{\infty} dk k^2 \bar{f}(k) \]
\[ - 4\pi e^2 \lambda_c \sum_k k^{-1} \bar{f}(k)e^{ik(r_a - R_a)} \]
\[ + \pi^{-1} e^2 \lambda_c \int_0^{\infty} dk k \bar{f}^2(k) \]
\[ + \sum_{a<b} d_{ai} \Gamma_{ij}(R^{eb}) d_{bj}. \]
The last term represents the interaction among the ED moments referring to different atoms, due both to the Coulomb field and to the modified transverse electric-field \( E^f_a \). The matrix \( \Gamma \) is given by
\[ \Gamma_{ij}(R) \]
\[ = -\frac{4\pi}{V} \sum_k e^{ikR} [1 - \bar{f}^2(k)](\delta_{ij} - \frac{k_i k_j}{k^2}) \]
\[ = (\delta_{ij} \nabla^2 - \delta_i \partial_j) \frac{4\pi}{V} \sum_k k^{-2} [1 - \bar{f}^2(k)]e^{ikR} \]
\[ \simeq (\delta_{ij} \nabla^2 - \delta_i \partial_j) \frac{2}{\pi} \int_0^{\infty} dk [1 - \bar{f}^2(k)] \frac{\sin kR}{kR} \]
\[ = (\delta_{ij} \nabla^2 - \delta_i \partial_j) \frac{2}{\pi R} \int_0^{\infty} dt [1 - \bar{f}^2(\frac{t}{R})] \frac{\sin t}{t}. \]
The leading contribution to this expression can be evaluated by use, in the calculation of the last integral, of the asymptotic expansion for \( \bar{f} \), given in eq.(3.9). We obtain
\[ \frac{2}{\pi R} \int_0^{\infty} dt [1 - \bar{f}^2(\frac{t}{R})] \frac{\sin t}{t} \]
\[ \simeq \frac{8(d^2)}{3\pi e^2 \lambda_c} \frac{1}{R^2} \int_0^{\infty} dt \sin t \frac{8(d^2)}{3\pi e^2 \lambda_c} R^{-2}, \] (4.7)
where the two contributions proportional to \( R^{-1} \) cancel each other. In this way, for the leading contribution to \( \Gamma_{ij} \) we obtain the expression
\[ \Gamma_{ij}(R) \sim \frac{16(d^2)}{3\pi e^2 \lambda_c} R^{-4}(\frac{4X_i X_j}{R^2} - \delta_{ij}). \] (4.8)
For example in the case of a pair of hydrogen atoms eq.(4.8) reads
\[ \Gamma_{ij}(R) \sim \frac{16}{\pi a^2}(\frac{a}{R})^4(4X_i X_j \frac{R^2}{R^2} - \delta_{ij}). \] (4.9)
Quite relevant in the $N$-atom case is the fact that the photon number of eq. (3.18) is multiplied by $N$. In fact a uniform distribution of $N$ atoms in a volume $V$ can be assumed as a rough representation for a refractive medium. In such a case, the number of photons per unit-volume would be given by
\[
\frac{N_{ph}}{V} \approx \frac{N}{V} \frac{\langle d^2 \rangle}{3 \pi \hbar c} \int_0^\infty dk k^2 f^2(k), \tag{4.10}
\]
with the following distribution with respect to the frequency $\omega$
\[
N_{ph}(\omega) \approx \frac{N}{V} \frac{\langle d^2 \rangle}{3 \pi \hbar c} \omega f^2(\omega/e). \tag{4.11}
\]
Assuming $N/V \approx 10^{23}$ $cm^{-3}$ and using the result of eq. (4.4) one obtains $N_{ph}/V \approx 10^{16}$ $cm^{-3}$. This result (very roughly) represents the total number of photons per cubed centimeter, which are present actually in a refractive medium in its ground state.

V. VAN DER WAALS POTENTIAL

The long-distance interaction between two neutral atom is due essentially to the van der Waals force. Up to the second order the perturbation theory gives an explicit expression for the dipole-dipole interaction energy. The standard calculation is based on the Coulomb interaction as given by the last term of eq. (4.3), with $g_{ij}$ given in eq. (4.4). The well-known result \[3\] is
\[
U'(R) \tag{5.1}
\]
\[
\approx \frac{6}{R^6} \sum_{b_1 b_2} \frac{|\langle b_1 | d_1^{(1)} | g \rangle|^2 |\langle b_2 | d_2^{(2)} | g \rangle|^2}{2E_0 - E_{b_1} - E_{b_2}},
\]
which is proportional to $R^{-6}$.

However in Sec.IV we have shown that the complete dipole-dipole interaction, is represented by the last term in eq. (4.5), where the matrix $g_{ij}$ is replaced by $\Gamma_{ij}$ of eq. (4.8) (or by eq. (4.9) for a pair of hydrogen atoms). As a consequence, the potential $U'$ of eq. (5.1) is replaced by
\[
U(R) \approx \frac{11}{R^6} \frac{16\langle d^2 \rangle}{3\pi e^2 \lambda_c} \tag{5.2}
\]
\[
\sum_{b_1 b_2} \frac{|\langle b_1 | d_1^{(1)} | g \rangle|^2 |\langle b_2 | d_2^{(2)} | g \rangle|^2}{2E_0 - E_{b_1} - E_{b_2}},
\]
which is proportional to $R^{-8}$.

The ratio of the two expressions is
\[
\frac{U(R)}{U'(R)} \approx \frac{11}{6R^2} \frac{16\langle d^2 \rangle}{3\pi e^2 \lambda_c}^2. \tag{5.3}
\]
For two hydrogen atoms eq. (5.3) reads
\[
\frac{U(R)}{U'(R)} \approx \frac{11}{6} \frac{a}{R} \frac{\alpha^2}{\pi \alpha^2} \approx 8.9 \times 10^6 \left(\frac{a}{R}\right)^2. \tag{5.4}
\]

Let us recall that both $U$ and $U'$ are negative. From eq. (5.4) one can see that $|U(R)| > |U'(R)|$, for $R < 9.4 \times 10^2 a$. Actually the experimental status does not look conclusive.

VI. CONCLUSION

We have shown that, in the ED representation, the correct Hamiltonian describing an atom interacting with the radiation field is given by eq. (2.24), with $\hat{f}$ given by eq. (3.8). Such an expression appears sensibly more complicated than the simple expression $-\mathbf{d} \cdot \mathbf{E}_L$, which is assumed usually.

We have analysed some consequences concerning namely the photon-distribution and the van der Waals interaction. In the last case we have obtained the remarkable result that, at large distance, the van der Waals potential between two atoms is proportional to $R^{-8}$. We are not aware of any direct measurement of the van der Waals potential, between two neutral polarizable atoms, especially at large distance. A wide bibliography on the van der Waals interaction can be found in Ref. \[6\].

Appendix A: Integrals

We outline the method used to calculate the integrals referring to the hydrogen atom. The integrals are either of the following type
\[
I_n(A) = \int_0^\infty dz \ (z^2 + A)^{-n}, \tag{A1}
\]
of the following one
\[
I_{nm}(A, B) = \int_0^\infty dz \ (z^2 + A)^{-n} (z + B)^{-m}, \tag{A2}
\]
with $n, m$ positive integers.

For $n > 1$ we have
\[
I_n(A) = (-)^{n-1} n! (n-1)!^{-1} \frac{\partial^{n-1}}{\partial A^{n-1}} I_1(A), \tag{A3}
\]
with
\[
I_1(A) = \int_0^\infty dz \ (z^2 + A)^{-1} = \frac{\pi}{2\sqrt{A}}. \tag{A4}
\]
In a similar way, for $n \geq 1$ and $m \geq 1$ we have
\[
I_{nm}(A, B) = \frac{(-)^{n+m-2} \partial^{m-1}}{\partial B^{m-1}} I_{11}(A, B), \tag{A5}
\]
The integral $I_{11}$ can be calculated by standard techniques. The result is
\[
I_{11}(A, B) = \int_0^\infty dz \ (z^2 + A)^{-1} (z + B)^{-1} \tag{A6}
\]
\[
= \left( A + B^2 \right)^{-1} \left[ \frac{\pi B}{2\sqrt{A}} + \frac{1}{2} \ln A - \ln B \right].
\]
At the end of the calculations one has to put $A = 1$ and $B = \alpha/4$.

---

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