

Single atom inside or outside a dielectric or metallic bubble

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The dispersive van der Waals energy of a ground-state atom encapsulated in, or placed in the vicinity of, a spherical dielectric or metallic shell is calculated. The treatment, the validity of which is restricted to the intermediate distance range, makes use of the random phase approximation and the propagator method. It is shown that the dielectric medium appears as a special case in the general nonlocal treatment used for a metal. Examples are presented and discussed. The interaction between an argon atom and a fullerene molecule, averaged over the molecule orientation and including a short-distance repulsive contribution, is calculated. It is then used to evaluate elastic differential cross sections at low energies (26 and 52 meV)—both of them exhibiting clear rainbow structures—and the total cross section in the range 10–100 meV.

I. INTRODUCTION

In a previous paper¹ the problem of a microsystem (ground-state atom or molecule) placed inside an empty spherical cavity in an infinite, linear, homogeneous, and isotropic medium has been addressed. While the treatment makes use of standard methods such as the random phase approximation (the atom is described as a sum of fluctuating electric moments)² and the propagator or susceptibility method,³ the fact that the medium extends to infinity gives rise to a special problem, namely, the determination of an adapted radial basis set able to provide converging physical quantities such as the induced polarization, the van der Waals atom-surface interaction, etc. This determination has been made by considering in a first step a medium limited by two concentric spheres of radii a, b , making then b infinite once the response potential of the medium has been calculated. This treatment naturally emerges into that of the case of an atom encapsulated inside a bubble. Actually as it will be seen further it includes as well the case of an atom outside the bubble, providing then a synthesis of the cases of a filled spheroid and of an empty cavity.⁴ In the following for sake of simplicity we shall restrict to a dipolar moment but the method can be easily extended to higher orders by using proper expansions of the source potential. The validity of the method is restricted to the intermediate distance range for the following reasons: (i) because of the quasistatic approximation, it does not take into account retardation effects which become significant at large distances (≥ 100 a.u.), (ii) at distances of a few au, electronic orbitals of the atom and the solid overlap, giving rise to a repulsive interaction, (iii) at such short distances the description of the solid as a continuous medium becomes questionable. When necessary, points (ii) and (iii) can be solved by summing the repulsive part of a Lenard-Jones potential over the solid atomic lattice.

Various applications of the situation considered in this paper can be found, some of them being nowadays investigated experimentally, such as the confinement of atoms or molecules inside micro sized bubbles or tubes^{5,6} (the present treatment could be readily extended to the cylindrical sym-

metry), atoms in the vicinity of a microsphere.⁷ The paper is organized as follows: in Sec. II the problem of an atom inside a bubble of radii a, b is considered. The response potentials of dielectric and metallic media are calculated and the propagators inside the bubble are determined. Finally the van der Waals energy is evaluated. The empty cavity is obtained by making b infinite. In Sec. III similar quantities as before, i.e., the response potential, the propagators outside the bubble and the energy are determined for an atom outside the bubble. The case of an atom in the vicinity of a filled spheroid is obtained by taking the limit $a \rightarrow 0$. Then it is shown in both cases that by making respectively a or b infinite one gets the due common limiting value of the energy which is that of a planar surface. Finally by making both a and b infinite, keeping finite the difference $b - a$, one obtains the dispersion energy of an atom placed in front of a plate of a finite thickness. In Sec. IV the collision of an atom (Ar) on a fullerene molecule assimilated to a bubble is studied as an example of the general treatment, a repulsive short range potential being added to the van der Waals energy.

II. AN ATOM INSIDE A BUBBLE

Let us consider a medium, which is assumed to be homogeneous, isotropic, and linear, limited by two concentric spheres S_a, S_b of radii a, b . The atom (dipole μ) is located at point \mathbf{R} inside the bubble ($R < a$), with \mathbf{R} collinear to the \hat{z} axis (see Fig. 1). Let ϕ_0, ϕ_1, ϕ_2 be the potentials at a specific frequency (ω), inside S_a , in between S_a and S_b , and outside S_b respectively. The basic quantity here, from which the propagators and all physical quantities will be deduced, is the so-called “response potential” of the medium, inside S_a , i.e., the difference $\phi_r = \phi_0 - \phi_s$, where ϕ_s is the source potential.

A. Response potential and inner reflection factors

1. Dielectric medium

Let us first assume that the medium is a neutral dielectric of permittivity $\varepsilon(\omega)$. In this case our method follows that

already used by Linder⁸ to treat a cavity in infinite dielectric medium and that used by Lucas *et al.* to treat a C_{60} molecule assimilated to a dielectric bubble⁹ (in this latter case the polarizability of the shell exhibits resonances corresponding to polarization waves). The treatment is greatly simplified by

$$\Delta_l^i(a, b, \omega) = \frac{[1 - \varepsilon(\omega)][1 + l + l\varepsilon(\omega)](l+1)(a^{2l+1} - b^{2l+1})}{[1 - \varepsilon(\omega)]^2 l(l+1)a^{2l+1} - [l + l\varepsilon(\omega) + 1][l + l\varepsilon(\omega) + \varepsilon(\omega)]b^{2l+1}}. \quad (1)$$

It is worth noticing that the limit

$$\lim_{b \rightarrow \infty} \Delta_l^i(a, b, \omega) = \frac{(l+1)[1 - \varepsilon(\omega)]}{(l+1)\varepsilon(\omega) + l} \quad (2)$$

coincides with the reflection factor previously given by Linder⁸ for a spherical cavity in an homogeneous isotropic dielectric medium.

The expression of Δ_l^i [Eq. (1)] is independent of the source under consideration. Dipole and higher multipole moments can be treated as well, by using proper expressions of the source potentials.

2. Metallic medium

The case of a dielectric medium is actually a rather simple electrostatic problem. The treatment of a metallic medium is more difficult, essentially because of the nonlocal character of the metal response. Whilst the following method could be extended to any type of source, for sake of clarity, we shall restrict ourselves to the case of a dipole moment μ located at a point $\mathbf{R}(0,0,R)$ inside the bubble ($R < a$).

At a specific frequency, any position-dependent quantity $g(\mathbf{r}, \omega)$ inside the metal can be expanded over the spherical harmonics

$$g(r, \omega) = \sum_{l,m} g_{lm}(r, \omega) Y_l^m(\Omega). \quad (3)$$

In view of simplifying the forthcoming treatment, the radial functions $g_{lm}(r, \omega)$ themselves are expanded over a complete and a orthogonal set of radial functions $f_{lm}(r, \omega)$, chosen in such a way that the products $F_{lm} = f_{lm} Y_l^m$ are solutions of a Helmholtz equation $(\Delta + k^2)F_{lm} = 0$.

This latter conditions implies that these radial basis functions are spherical Bessel functions, independent of m and they are *a priori* nonregular at the origin (which is located outside the medium):

$$f_l(kr) = \alpha_l j_l(kr) + \beta_l y_l(kr). \quad (4)$$

It is easily verified that if the Wronskian of two such functions vanishes at $r=a$ and $r=b$ which is obtained here by imposing the two conditions

$$\partial_x f_l(x) \Big|_{x=ka, kb} = 0, \quad (5)$$

then the orthogonality property holds. Equation (5) determines the coefficients α_l, β_l in Eq. (4) as well as a set of

the local character of the response of the medium.

A standard method using expansions over the spherical harmonics, the Laplace equation and the boundary conditions, leads to the inner reflection factor for a specific spherical harmonic Y_l^m :

discrete k values. Another orthogonality property, related to two different values of k , also holds

$$\int_a^b dr r^2 f_l(kr) f_l(k'r) = \frac{1}{N_{kl}^2} \delta_{kk'}, \quad (6)$$

where the normalizing factors N_{kl} are given by

$$\frac{1}{N_{kl}^2} = \frac{1}{2} \{ b^3 [f_l^2(kb) - f_{l-1}(kb) f_{l+1}(kb)] - a^3 [f_l^2(ka) - f_{l-1}(ka) f_{l+1}(ka)] \}. \quad (7)$$

The expansion of radial quantities $g_{lm}(r, \omega)$ over this basis is

$$g_{lm}(r, \omega) = \sum_k N_{kl} f_l(kr, \omega) \tilde{g}_{lm}(k, \omega), \quad (8a)$$

where

$$\begin{aligned} \tilde{g}_{lm}(k, \omega) &= N_{kl} \int_V d^3 r f_l(kr) Y_l^{m*}(\Omega) g(\mathbf{r}, \omega) \\ &= N_{kl} \int_a^b dr r^2 f_l(kr) g_{lm}(r, \omega), \end{aligned} \quad (8b)$$

V being the volume in between the spheres S_a, S_b .

Inside the metal the potential $\phi_1(\mathbf{r}, \omega)$ obeys the Poisson equation

$$\Delta \phi_1(\mathbf{r}, \omega) = -4\pi \delta\rho(\mathbf{r}, \omega), \quad (9)$$

there $\delta\rho$ is the charge density at point \mathbf{r} . Assuming a linear response of the medium this charge density is related to ϕ_1 by¹⁰

$$\delta\rho(\mathbf{r}, \omega) = \int_V d^3 r' \chi(\mathbf{r}, \mathbf{r}', \omega) \phi_1(\mathbf{r}', \omega), \quad (10)$$

where $\chi(\mathbf{r}, \mathbf{r}', \omega)$ is a nonlocal generalized susceptibility.

Using the transformation (8b), once for $\delta\rho$ and ϕ_1 and twice for χ , Eq. (10) transforms into the matrix equation

$$\delta\tilde{\rho}_{lm}(k, \omega) = \sum_{l', m', k'} \tilde{\chi}_{ll' mm'}(k, k', \omega) \phi_{1l'm}(k', \omega), \quad (11)$$

where

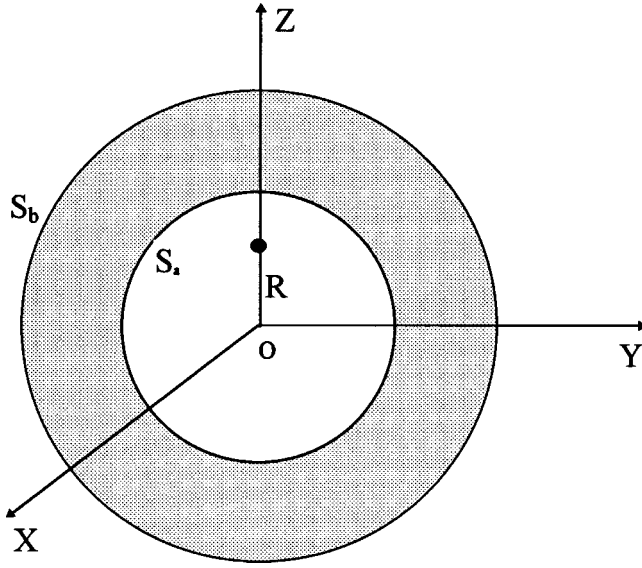


FIG. 1. Geometry of the problem: an atom is located at a distance R from the center O of a bubble limited by two concentric spheres of radii a, b ($R \leq a$ or $R \geq b$).

$$\begin{aligned} \bar{\chi}_{ll'mm'} = & N_{kl} N_{k'l'} \int_V d^3 r \int_V d^3 r' f_l(kr) f_{l'}(k'r') Y_{l'm'}^{m'}(\Omega') \\ & \times Y_{l'm}^{m*}(\Omega) \chi(\mathbf{r}, \mathbf{r}', \omega). \end{aligned} \quad (12)$$

The same transformation applied to Eq. (9) leads to

$$-4\pi \delta \bar{\rho}_{lm} = N_{kl} \int_V d^3 r f_l(kr) Y_{l'm}^{m*}(\Omega) \Delta \phi_1(\mathbf{r}, \omega). \quad (13)$$

By using the Green's identity,¹¹ the volume integral in Eq. (13) can be expressed as

$$\frac{-k^2}{N_{kl}} \bar{\phi}_{1,lm}(k, \omega).$$

Finally Eqs. (11) and (13) lead to a self-consistency equation for the potentials $\bar{\phi}_{1,lm}$ in k space, namely,

$$\begin{aligned} \sum_{l', m', k'} [4\pi \bar{\chi}_{ll'mm'}(k, k', \omega) - k^2 \delta_{ll'} \delta_{mm'} \delta_{kk'}] \bar{\phi}_{1, l'm'}(k', \omega) \\ = N_{kl} [a^2 f_l(ka) \phi'_{1,lm}(a, \omega) - b^2 f_l(kb) \phi'_{1,lm}(b, \omega)], \end{aligned} \quad (14)$$

where the (unknown) radial derivatives $\phi'_{1,lm}$ are defined by

$$\phi'_{1,lm}(a, \omega) = \int d\Omega Y_{l'm}^{m*}(\Omega) \partial_r \phi_1(\mathbf{r}, \omega) \Big|_{r=a} \quad (15)$$

and a similar definition at $r=b$.

Owing to the isotropy and spherical symmetry of the metal, the susceptibility matrix simplifies into¹²

$$\bar{\chi}_{ll'mm'}(k, k', \omega) = \bar{\chi}_l(k, k', \omega) \delta_{ll'} \delta_{mm'}. \quad (16)$$

Let Ξ be the "dielectric" matrix the elements k, k' of which are

$$\Xi_l(k, k', \omega) = k^2 \delta_{kk'} - 4\pi \bar{\chi}_l(k, k', \omega). \quad (17)$$

It contains all the information about the dynamical properties of the metal. Using Ξ , Eq. (14) leads to a set of linear equations in $\bar{\phi}_{1,lm}(k, \omega)$ which can be solved by introducing the inverse matrix Ξ^{-1} :

$$\begin{aligned} \bar{\phi}_{1,lm}(k, \omega) = \sum_{k'} N_{k'l} [b^2 f_l(k'b) \phi'_{1,lm}(b, \omega) \\ - a^2 f_l(ka) \phi'_{1,lm}(a, \omega)] \Xi_l^{-1}(k, k', \omega). \end{aligned} \quad (18)$$

This leads to the expression of the potential inside the metal

$$\begin{aligned} \phi_1(\mathbf{r}, \omega) = \sum_{lm} [G_l(r, \omega) \phi'_{1,lm}(b, \omega) \\ - F_l(r, \omega) \phi'_{1,lm}(a, \omega)] Y_l^m(\Omega), \end{aligned} \quad (19)$$

where

$$F_l(r, \omega) = a^2 \sum_{k,k'} N_{kl} N_{k'l} f_l(kr) f_l(k'a) \Xi_l^{-1}(k, k', \omega), \quad (20a)$$

$$G_l(r, \omega) = b^2 \sum_{k,k'} n_{kl} N_{k'l} f_l(kr) f_l(k'b) \Xi_l^{-1}(k, k', \omega). \quad (20b)$$

The only unknown quantities in Eq. (19) are the radial derivatives $\phi'_{1,lm}$. These can be derived from the continuity conditions at boundaries S_a, S_b . The response potential ϕ_r , the source potential ϕ_s inside the bubble, and the outer potential ϕ_2 have the same type of expansion as they had in the case of a dielectric medium. Using the following expansion of the potential ϕ_0 inside the bubble:

$$\phi_0(\mathbf{r}, \omega) = \sum_{l,m} (A_{l,m} r^{-l-1} + B_{l,m} r^l) Y_l^m(\Omega) \quad (21)$$

and writing the continuity of the potential and of its gradient at boundaries S_a, S_b , the radial derivatives are eliminated and one gets

$$B_{lm}(a, b, \omega) = \Delta_l^i(a, b, \omega) \frac{1}{a^{2l+1}} A_{lm}, \quad (22)$$

where the A_{lm} 's are the coefficients in the source potential expansion.

The new nonlocal inner reflection factor is

$$\Delta_l^i(a, b, \omega) = \frac{(l+1)^2 G_l(a, \omega) F_l(b, \omega) + [b + (l+1) G_l(b, \omega)] [a - (l+1) F_l(a, \omega)]}{l(l+1) G_l(a, \omega) F_l(b, \omega) - [b + (l+1) G_l(b, \omega)] [a + l F_l(a, \omega)]}. \quad (23)$$

From Eq. (22) one readily gets the response potential

$$\phi_r(\mathbf{r}, \omega) = \sum_{lm} \Delta_l^i(a, b, \omega) A_{lm} \frac{r^l}{a^{2l+1}} Y_l^m(\Omega). \quad (24)$$

It may be noticed that, because of their normalization [Eqs. (20)] the functions F_l and G_l remain finite when $b \rightarrow \infty$. As a consequence

$$\lim_{b \rightarrow \infty} \Delta_l^i(a, b, \omega) = \frac{(l+1)F_l(a, \omega) - a}{lF_l(a, \omega) + a}. \quad (25)$$

This is exactly the reflection factor $\Delta_l(a, \omega)$ already obtained¹ for a spherical cavity in an infinite metal.

It is obviously a great advantage to have a general analytical expression of the nonlocal reflection factors [Eqs. (20a), (20b), (23)]. A dielectric local medium naturally ap-

pears as a particular case of this result, namely the case in which the inverse dielectric matrix elements have the local form

$$\Xi_l^{-1}(k, k', \omega) = \frac{1}{k^2 \varepsilon(\omega)} \delta_{kk'}. \quad (26)$$

Indeed under such condition, one obtains

$$F_l(r, \omega) = \frac{a^2}{\varepsilon(\omega)} \sum_k \frac{N_{kl}^2}{k^2} f_l(kr) f_l(ka), \quad (27a)$$

$$G_l(r, \omega) = \frac{b^2}{\varepsilon(\omega)} \sum_k \frac{N_{kl}^2}{k^2} f_l(kr) f_l(kb). \quad (27b)$$

After some calculation, the expression of $\Delta_l^i(a, b, \omega)$ takes the simplified form

$$\Delta_l^i(a, b, \omega) = \frac{(l+1)[1 - \varepsilon(\omega)][l\varepsilon(\omega) + l + 1](a^{2l+1} - b^{2l+1})}{l(l+1)[1 - \varepsilon(\omega)]^2 a^{2l+1} - [l\varepsilon(\omega) + l + 1][(l+1)\varepsilon(\omega) + l]b^{2l+1}} \quad (28)$$

which is the inner reflection factor calculated previously for a dielectric medium [Eq. (1)].

B. Propagators inside the bubble; van der Waals energy

Let $\underline{E}^{(n)}(r, \omega)$ be the n th order tensorial gradient of the response potential $\phi_r(r, \omega)$ defined by Eq. (24):

$$\underline{E}^{(n)}(\mathbf{r}, \omega) = -(\nabla)^n \phi_r(\mathbf{r}, \omega), \quad (29)$$

In a general case ϕ_r is a sum of contributions related to the different moments $\underline{M}^{(m)}(\omega)$ (dipole for $m=1$, quadrupole for $m=2$, etc.) present at the source point \mathbf{R} . The so-called propagator or electric susceptibility is a tensor of rank $(n+m)$ allowing to derive $\underline{E}^{(n)}(\mathbf{r}, \omega)$ from $\underline{M}^{(m)}(\omega)$ by

$$\underline{E}^{(n)}(\mathbf{r}, \omega) = - \sum_{m=1} \frac{1}{(2m-1)!!} {}^n \underline{\mathcal{G}}^m(\mathbf{r}, \mathbf{R}, \omega) [m] \underline{M}^{(m)}(\omega), \quad (30)$$

where $[m]$ indicates the contraction order.

In the present case we shall restrict to the ‘‘dipolar propagator’’ ($n=1$) for a dipole source ($m=1$) which in general largely dominates (higher order propagators could be determined in a similar way¹³). It is readily derived from Eq. (24). It has a standard form, apparently similar to that obtained elsewhere.^{1,7} Nevertheless one has to keep in mind that the specificity of the physical problem is contained in the reflection factors Δ_l^i :

$${}^1 \underline{\mathcal{G}}^1(\mathbf{r}, \mathbf{R}, \omega) = - \sum_{lm} \underline{T}_{lm}^{(1)} \frac{r^{l-1}}{a^{2l+1}} \Delta_l^i(a, b, \omega) \underline{Q}^{(1)} Y_l^m(\Omega), \quad (31)$$

where the components of $\underline{T}_{lm}^{(1)}$ are

$$\begin{aligned} [\underline{T}_{lm}^{(1)}]_x &= \frac{\beta_l}{\sqrt{2}} [C(l, 1, l-1/1, -1, 0) \delta_{m,1} \\ &\quad - C(l, 1, l-1/-1, 1, 0) \delta_{m,-1}], \\ [\underline{T}_{lm}^{(1)}]_y &= -i \frac{\beta_l}{\sqrt{2}} [C(l, 1, l-1/1, -1, 0) \delta_{m,1} \\ &\quad + C(l, 1, l-1/-1, 1, 0) \delta_{m,-1}], \\ [\underline{T}_{lm}^{(1)}]_z &= \beta_l C(l, 1, l-1/0, 0, 0) \delta_{m,0}. \end{aligned} \quad (32)$$

$\underline{Q}^{(1)}$ is a Cartesian tensor of rank 1, acting on angular functions according to

$$-\nabla[r^l Y_l^m(\Omega)] = r^{l-1} \underline{Q}^{(1)} Y_l^m(\Omega). \quad (33)$$

The fluctuating dipole moment μ of the atom can be derived from the electric field using the atomic polarizability tensor ${}^1 \underline{\alpha}^1(\omega)$ the elements of which are

$${}^1 \alpha_{ij}^1(\omega) = \alpha(\omega) \delta_{ij} \quad (i, j = x, y, z). \quad (34)$$

The van der Waals energy is given by¹⁴

$$U^{(1)}(\mathbf{R}) = \frac{\hbar}{2\pi} \int_0^\infty d\xi {}^1 \underline{\alpha}^1(i\xi) [2] {}^1 \underline{\mathcal{G}}^1(\mathbf{R}, \mathbf{R}, i\xi). \quad (35)$$

Using Eq. (31) one obtains

$$U^{(1)}(R) = \sum_{l \geq 1} C_l(a, b) \frac{R^{2l-2}}{a^{2l+1}}, \quad (36a)$$

where

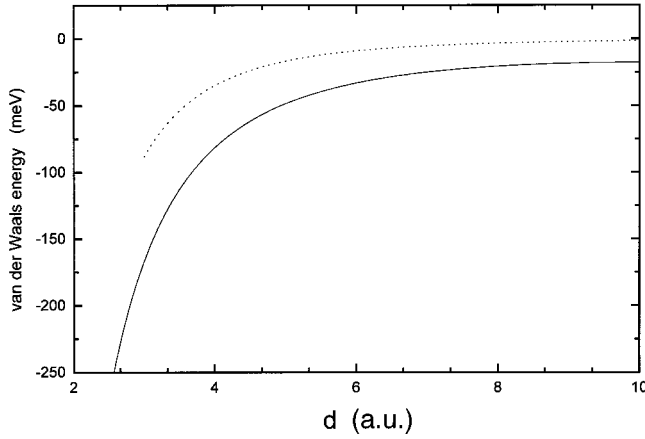


FIG. 2. full line: van der Waals energy $U^{(1)}$ for an argon atom inside a LiF bubble ($a=10$ a.u., $b=20$ a.u.) as a function of the distance d to the inner sphere; broken line: $U^{(1)}$ for an Ar atom outside the bubble, as a function of d , which is now the distance to the outer sphere. The inner energy is lower than the outer one, which is an evidence for a confinement effect (Ref. 27).

$$C_l(a,b) = \frac{\hbar}{2\pi} l(2l+1) \int_0^\infty d\xi \Delta_l^i(a,b,i\xi) \alpha(i\xi). \quad (36b)$$

The numerical calculation of this energy makes use of (i) the atomic polarizability $\alpha(\omega)$, which can be obtained, for instance, from the Drude's model

$$\alpha(\omega) = \alpha(0) \omega_a^2 (\omega_a^2 - \omega^2)^{-1} \quad (37)$$

and (ii) the reflection factors $\Delta_l^i(a,b,\omega)$ given either by formula (1) for a dielectric, or Eq. (23) for a metal.

The "dielectric" matrix Ξ_l of a metal is related to the so-called Lindhard function¹⁵ $\varepsilon(k,\omega)$ by $\Xi_l(k,k',\omega) = k^2 \varepsilon(k,\omega) \delta_{kk'}$. In most cases a realistic analytical form of $\varepsilon(k,\omega)$ can be derived from the hydrodynamical model of Fuchs and Claro:¹⁶

$$\varepsilon(k,\omega) = 1 - \frac{\omega_p^2}{\omega^2 - \delta^2 k^2}, \quad (38)$$

where ω_p is the plasmon frequency; δ is a parameter characteristic of the electronic screening effect inside the metal, which is close to the Fermi velocity at high frequency.

In the case of a dielectric medium, the permittivity function $\varepsilon(\omega)$ is given the Clausius-Mossotti formula

$$\varepsilon(\omega) = \left[1 + g_0 \frac{\omega_0^2}{\omega_0^2 - \omega^2} \right] \left[1 - g_0 \frac{\omega_0^2}{\omega_0^2 - \omega^2} \right]^{-1}. \quad (39)$$

Some examples are presented here. In Fig. 2 (full line), $U^{(1)}$ is plotted as a function of d , the distance from the dipole source to the inner sphere, for an Ar atom in a LiF bubble ($a=10$ a.u., $b=20$ a.u.). Atom and dielectric parameters are as follows:¹⁷

$$\begin{aligned} \alpha(0) &= 11.09 \text{ a.u.}; & \omega_a &= 0.7024 \text{ a.u.}; \\ g_0 &= 0.32 \text{ a.u.}; & \omega_0 &= 0.639 \text{ a.u.} \end{aligned}$$

In Fig. 3 the same system is studied for fixed values of a

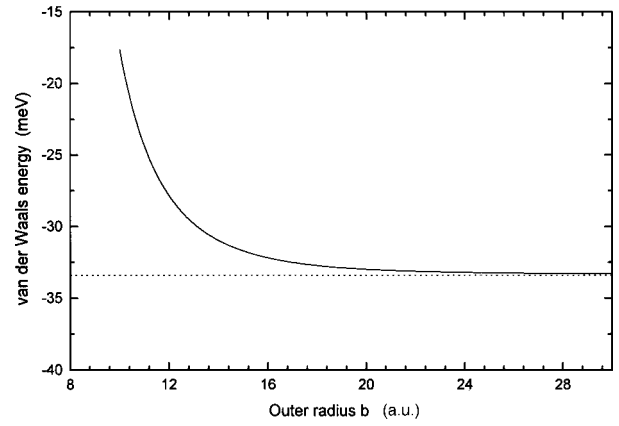


FIG. 3. $U^{(1)}$ as a function of the outer radius b ; $a=10$ a.u.; $R=4$ a.u. The asymptotic value at large b corresponds to an atom inside a spherical cavity in an infinite medium (broken line).

($=10$ a.u.) and $R=a-6$ a.u. The energy is plotted as a function of b ($b \geq a$). It is seen that $U^{(1)}$ approaches its limiting value i.e., the energy corresponding to a spherical cavity in an infinite medium at relatively low values of b (b larger than 25 a.u.), which shows that the effect induced by the source in the solid is actually restricted to a rather thin spherical sheet.

It may be noticed that the usual form of the van der Waals energy for an atom in front of an infinite medium limited by a planar surface is readily recovered from Eqs. (36a) and (36b) by making b infinite, and both a and R infinite with the condition that $d=a-R$ remains finite. Under such conditions the problem becomes axially symmetric which implies the predominance of l values much larger than 1. Consequently $\Delta_l^i \approx (1-\varepsilon)/(1+\varepsilon)$ and $C_l \approx (\hbar/2\pi) l(2l+1)D$, where

$$D = \int_0^\infty d\xi \frac{1-\varepsilon(i\xi)}{1+\varepsilon(i\xi)} \alpha(i\xi).$$

Finally one gets

$$\begin{aligned} U^{(1)} &\approx \frac{1}{aR^2} \frac{\hbar}{\pi} D \sum_l l \left(l + \frac{1}{2} \right) \left(\frac{R}{a} \right)^{2l} \\ &\approx \frac{1}{aR^2} \frac{\hbar}{\pi} \int_0^\infty dl l^2 \left(\frac{R}{a} \right)^{2l} \\ &= \frac{\hbar}{4\pi} D \frac{1}{d^3}. \end{aligned} \quad (40)$$

A similar calculation provides the van der Waals energy of an atom placed at a distance d in front of a dielectric plate of thickness e . This situation corresponds to a , b , and R infinite, $b-a=e$ and $a-R=d$ remaining finite. In Fig. 4 this energy, calculated for the system Ar+LiF, is plotted as a function of the thickness e , the distance being fixed at $d=6$ a.u. The asymptotic value of $U^{(1)}$ at large e coincides with the energy of the atom in front of an infinite medium limited by a plane. As expected $U^{(1)}=0$ at $e=0$. At small values of e , $U^{(1)}$ has a linear dependence on e :

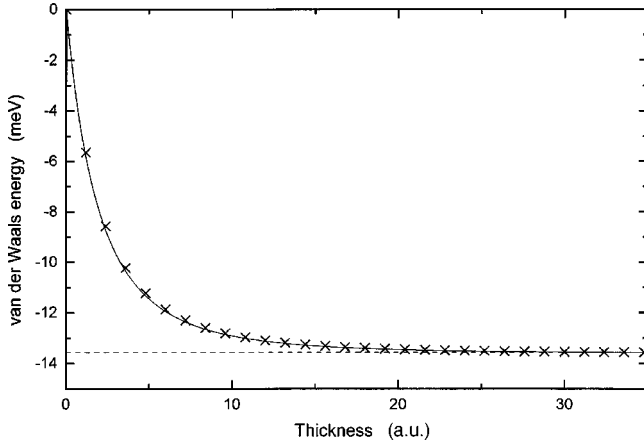


FIG. 4. $U^{(1)}$ for an argon atom at a distance $d=6$ a.u. from a LiF plate, as a function of the thickness e of the plate. The result is obtained as a limiting case ($a \rightarrow \infty$; $b \rightarrow \infty$; $b-a=e$) of an atom either inside the bubble (full line) or outside the bubble (crosses). The horizontal broken line corresponds to a semi-infinite medium limited by a plane.

$$U^{(1)} \approx \frac{3\hbar}{\pi} \Gamma \frac{e}{d^4}, \quad \text{where } \Gamma = - \int_0^\infty d\xi \frac{[1 - \varepsilon(i\xi)]^2}{4\varepsilon(i\xi)} \alpha(i\xi).$$

These results are in qualitative agreement with those obtained by Schmeits and Lucas¹⁸ for an atom in the vicinity of an aluminum film.

In Fig. 5, an example of a nonlocal treatment, for an argon atom inside a silver spherical shell ($a = 10$ a.u., $b = 20$ a.u.) is shown. The calculation uses the same atom parameters as before. For the metal, the parameters involved in the hydrodynamical Lindhard function [Eq. (38)] are as follows:¹⁹ $\omega_p = 0.845$ a.u., $\delta = 1.031$ a.u. The van der Waals energy is plotted as a function of the distance d to the inner sphere (full line). It is compared to that given by a calculation using a local response (broken line). This latter energy is much lower than the nonlocal one which clearly shows the necessity to take in account the nonlocality of the response. The present model is rather crude. Much more elaborated models of the metal have been proposed.²⁰ In most cases they have

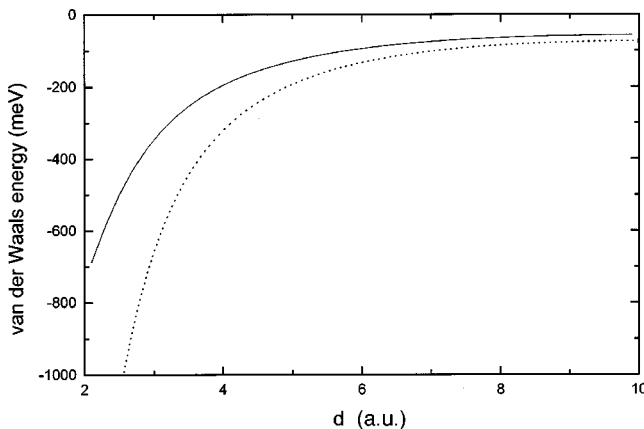


FIG. 5. $U^{(1)}$ for an argon atom inside a silver bubble ($a=10$ a.u., $b=20$ a.u.) as a function of d the distance to the inner sphere: full line: non-local calculation; broken line: local calculation.

been shown to give results close to those of the present model, particularly for large size solids.

III. AN ATOM OUTSIDE A BUBBLE

The atom dipole μ is located at point \mathbf{R} outside S_b ($R > b$). We keep the previous definitions of the potentials at a specific frequency ω : ϕ_0 inside S_a , ϕ_1 in the medium, ϕ_2 outside S_b . Now the response potential is $\phi_r = \phi_2 - \phi_s$, ϕ_s being the source potential.

A. Response potential and outer reflection factors

The treatment of a metallic medium is made as previously in the framework of the linear response. The potential ϕ_0 inside S_a , as well as the source potential ϕ_s (for $r > R$) and the response potential ϕ_r obey the Laplace equation. These potential can be expanded as

$$\begin{aligned} \phi_0 &= \sum_{lm} B_{lm} r^l Y_l^m(\Omega), \\ \phi_s &= \sum_{lm} E_{lm} r^l Y_l^m(\Omega), \end{aligned} \quad (41)$$

$$\phi_r = \sum_{lm} H_{lm} r^{-l-1} Y_l^m(\Omega),$$

the potential outside S_b being $\phi_2 = \phi_s + \phi_r$.

Inside the medium the potential obeys the Poisson equation

$$\Delta \phi_1(\mathbf{r}, \omega) = -4\pi \delta \rho(\mathbf{r}, \omega).$$

Using the linearity of the response, together with the transformation (8)–(10), one gets an expression of ϕ_1 identical to Eq. (19), where the functions $G_l(r, \omega)$, $F_l(r, \omega)$ have the same expressions as before [Eqs. (20a) and (20b)]. The continuity condition of the potential and its gradient at boundaries S_a , S_b allows us to eliminate the radial derivatives $\phi'_{l,m}$ (a or b, ω), which leads to the relation

$$H_{lm} = \Delta_l^0(a, b, \omega) E_{lm}. \quad (42)$$

The outer reflection factor Δ_l^0 is given by

$$\Delta_l^0(a, b, \omega) = \frac{lU - V}{(l+1)U - V}, \quad (43a)$$

where

$$\begin{aligned} U &= aG_l(b, \omega) + l[F_l(a, \omega)G_l(b, \omega) - F_l(b, \omega)G_l(a, \omega)], \\ V &= b[a + lF_l(a, \omega)]. \end{aligned} \quad (43b)$$

It may be noticed that the limiting expression of Δ_l^0 when a tend to zero is

$$\Delta_l^0(0, b, \omega) = \frac{lG_l(b, \omega) - b}{(l+1)G_l(b, \omega) + b}, \quad (44)$$

where

$$G_l(r, \omega) = b^2 \sum_{k, k'} N_{kl} N_{k'l} j_l(kr) j_l(k'r) \Xi_l^{-1}(k, k', \omega).$$

This coincides with the reflection factor obtained in Ref. 21 for a filled spheroid of radius b .

Using expressions (43a) and (43b) of the reflection factor, one readily obtains the response potential outside S_b :

$$\phi_r(\mathbf{r}, \omega) = \sum_{l, m} \Delta_l^0(a, b, \omega) \frac{b^{2l+1}}{r^{l+1}} E_{lm}(\omega) Y_l^m(\Omega). \quad (45)$$

In the present case of a dipolar source, the coefficients $E_{lm}(\omega)$ are given by

$$E_{lm}(\omega) = \beta_l \sum_{\alpha} C(l, 1, l+1/\alpha, -\alpha, 0) \delta_{m\alpha} \mu^{(-\alpha)}, \quad (46)$$

where $\alpha = -1, 0, +1$; C is a Clebsch Gordan coefficient and

$$\beta = \sqrt{4\pi(l+1)} R^{-l-2} \quad (R > b). \quad (47)$$

As previously the (local) dielectric medium appears as a special case of this nonlocal calculation. By making ‘‘local’’ the inverse matrix Ξ_l^{-1} [Eq. (26)]:

$$\Xi_l^{-1}(k, k', \omega) = \frac{\delta_{kk'}}{k^2 \varepsilon(\omega)},$$

one gets simplified expressions of the functions F_l and G_l [See Eqs. (27a) and (27b)].

After a rather tedious calculation one gets

$$\Delta_l^0(a, b, \omega) = \frac{[1 - \varepsilon(\omega)] l [l + (l+1)\varepsilon(\omega)] (a^{2l+1} - b^{2l+1})}{[(l+1)\varepsilon(\omega) + l][l + 1 + l\varepsilon(\omega)] b^{2l+1} - l(l+1)[\varepsilon(\omega) - 1]^2 a^{2l+1}}, \quad (48)$$

i.e., the reflection factor for a dielectric shell as it might be directly calculated by use of a standard method.

B. Propagators and van der Waals energy

Using a method similar to that of Sec. II B, one gets the dipolar propagator for a dipole source

$${}^1\mathcal{G}^1(\mathbf{r}, \mathbf{R}, \omega) = - \sum_{lm} \mathcal{T}_{lm}^{(1)} \frac{a^{2l+1}}{r^{2l+1}} \Delta_l^0(a, b, \omega) \mathcal{Q}^{(1)} Y_l^m(\Omega), \quad (49)$$

where the components of $\mathcal{T}_{lm}^{(1)}$ are now

$$[\mathcal{T}_{lm}^{(1)}]_x = \frac{\beta_l}{\sqrt{2}} [C(l, 1, l+1/2, -1, 0) \delta_{m,1} - C(l, 1, l+1/2, 1, 0) \delta_{m,-1}], \quad (50)$$

$$[\mathcal{T}_{lm}^{(1)}]_y = -i [\mathcal{T}_{lm}^{(1)}]_x, \quad (51)$$

$$[\mathcal{T}_{lm}^{(1)}]_z = \beta_l C(l, 1, l+1/0, 0, 0) \delta_{m,0}, \quad (52)$$

where β_l is given by Eq. (47) and

$$-\nabla[r^{-(l+1)} Y_l^m(\Omega)] = r^{-(l+2)} \mathcal{Q}^{(1)} Y_l^m(\Omega). \quad (53)$$

The van der Waals energy is again given by Eq. (35), which leads to

$$U^{(1)}(R) = \sum_{l \geq 1} C_l(a, b) \frac{a^{2l+1}}{R^{2l+4}}, \quad (54a)$$

where

$$C_l(a, b) = \frac{\hbar}{2\pi} (l+1)(2l+1) \int_0^\infty d\xi \Delta_l^0(a, b, i\xi) \alpha(i\xi). \quad (54b)$$

Numerical calculations have been made for the same system as before, namely, an argon atom outside a LiF bubble (the parameters used in the calculation have been already given in Sec. II B). In Fig. 2 (broken line), the energy $U^{(1)}$ is plotted as a function of the distance d to the outer sphere, for $a = 10$ a.u., $b = 20$ a.u. As expected $U^{(1)}$ tends to $-\infty$ as d approaches 0, and it tends to zero at infinite d . In a second calculation, $b = 20$ au and $d = 6$ au are kept constant whereas a is varied from zero to b (see Fig. 6). For $a = 0$ one recovers the value of $U^{(1)}$ of an atom outside a filled spheroid. On the other hand, as expected, for $a = b$, $U^{(1)} = 0$. Finally, making a , b , and R infinite, with both $b - a = e$ and $R - b = d$ finite, we are able to recalculate the energy of the atom in front of a plate. As it is seen in Fig. 4 (crosses), the result is identical to that already obtained on the inner side of the bubble.

IV. APPLICATION: THE COLLISION OF AN ARGON ATOM WITH A FULLERENE MOLECULE

In this last part we consider a collision between a ground-state argon atom and a C_{60} molecule translationally and vibrationally at rest. The collision energy lies in the subthermal to thermal range (a few tens of meV). Having in mind to calculate the Ar- C_{60} interaction by using the previous method, we first have to examine the validity of a model in which the fullerene molecule is assimilated to a bubble (see Ref. 22). Moreover because of the short distances involved in such a collision, repulsive terms have clearly to be added to the van der Waals energy. Nevertheless in a realistic collision experiment (e.g., a Ar beam passing through C_{60} vapor, or crossing a C_{60} beam) (i) the orientations of the target

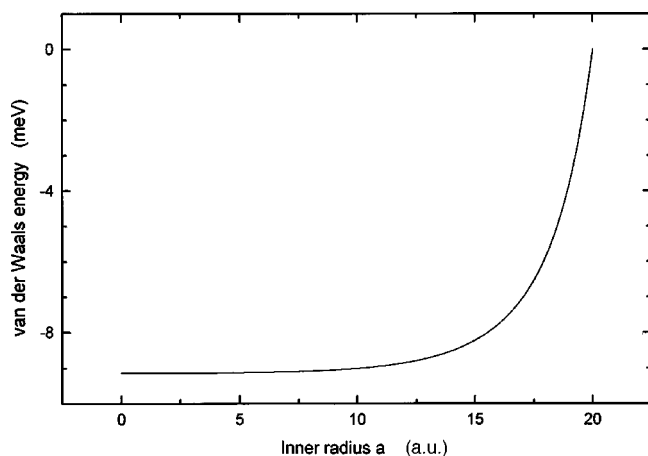


FIG. 6. $U^{(1)}$ as a function of the inner radius a ; $b=20$ a.u.; $R=24$ a.u. The value at $a=0$ corresponds to an atom outside a filled spheroid (Ar-LiF system).

molecules at a given time are random and (ii) these molecules are rotating. To take into account the point (i) would impose the difficult task to calculate (using an anisotropic potential) the differential cross section for a given orientation and then average this cross section over all molecular orientations. On another hand the point (ii) turns out to be an advantage, provided that the rotation is sufficiently fast compared to the relative Ar- C_{60} motion. In such a case it is justified to average the interaction *potential* (attractive and repulsive parts) over the molecule orientations, which leads to a simple spherical potential. The rotational constant of C_{60} can be estimated to be 7.46×10^{-9} atomic unit. As a consequence at 300 K, the mean value of the angular momentum J is about 1380, which corresponds to a rotation period $T=7.32$ ps. At a collision energy of 26 meV, the velocity of an argon atom is 317 m/s. The potential range being estimated at 30 atomic unit, the collision time is about 4.70 ps, i.e., slightly smaller than T , which seems to compromise the approximation mentioned above. However the anisotropy of the potential is periodic or quasiperiodic as a function of the rotation angle with a period largely smaller than 2π . Under such conditions it seems to be justified to average the potential and consider the C_{60} molecule as a bubble, at least for

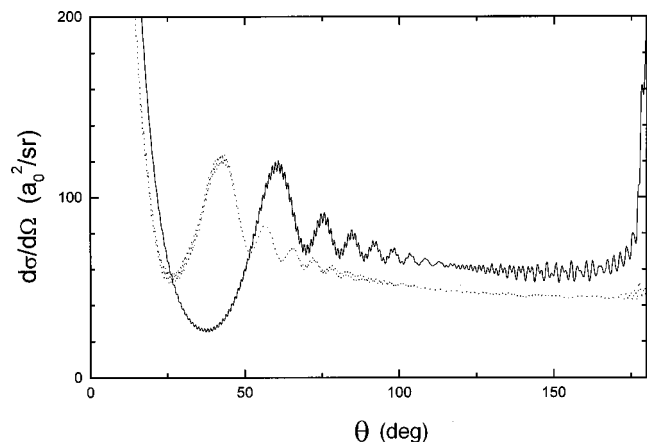


FIG. 7. Ar- C_{60} elastic differential cross sections in a_0^2/sr at 26 meV (full line) and 52 meV (dotted line). A rainbow effect is visible on both curves.

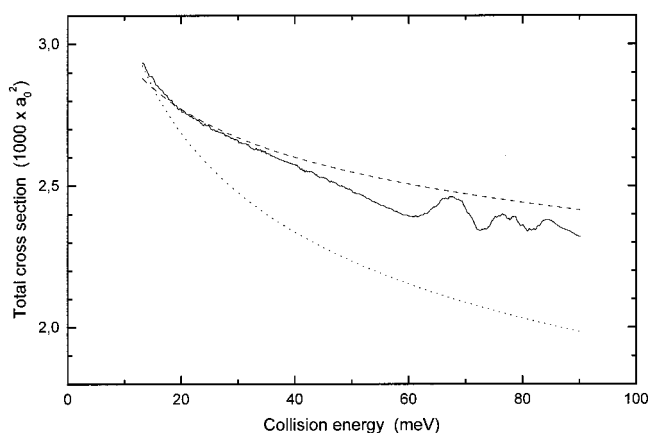


FIG. 8. Ar- C_{60} total elastic cross section in a_0^2 as a function of the collision energy E . The cross section tends to behave as $E^{-0.2}$ (potential in r^{-6}) at low energy (dotted line) and as $E^{-1/11}$ (potential in r^{-12}) at large energy (broken line). A glory structure is seen.

collision energies smaller than 100 meV. The mean repulsive part of the potential can be evaluated by summing the r^{-12} part of a Lenard-Jones potential over the volume of the material. The complete averaged potential has been calculated using the data of Refs. 23–25. It is in good agreement with that of Ref. 25. The barrier in between inner and outer regions is high enough to prevent any tunnel effect, at least at the collision energies considered here. As a consequence the collision treatment only involves the outer potential. Similarly the lower bound states of an atom inside the bubble (within a well of depth -388.2 meV at a distance of $4.37a_0$) are disconnected from outside: they are very close to those already found inside a spherical cavity in an infinite medium.¹ Obviously at large collision energy and/or low C_{60} rotational temperature the approximation of the mean potential fails, leading to a very interesting but difficult problem, namely, the penetration of an outer atom into C_{60} , followed by a delayed ejection, a process accompanied by a transfer of angular momentum to the molecule.

The shortness of the de Broglie wave length ($\lambda=0.63$ a.u. at 26 meV) fully justifies the use of the JWKB approximation. Phase shifts have been calculated for various collision energies, over the range 0–600 of the relative angular momentum l . Differential cross sections calculated at 26 and 52 meV are shown in Fig. 7. Rainbow structures due to the potential well are clearly seen. Because of the presence of an empty inner part which repels the potential well minimum (-158 meV) at a relatively large distance ($11.1a_0$), both the magnitude of the differential cross sections and the location of the rainbows should make it *relatively easy to experimentally observe these effects*, which would provide a severe test of the well parameters. On the other hand the total cross section as a function of the collision energy E (Fig. 8) reflects the behavior of the potential at mean and large distances. Towards low energies the cross section approaches a behavior in $E^{-1/5}$ characteristic of the expected long range potential in r^{-6} , whereas at larger energies it exhibits a glory oscillation (Fig. 8) around a mean value decreasing slower (roughly in $E^{-1/11}$, characteristic of a potential in r^{-12}) than it did at low energy. All these features should be observed in an experiment in which the attenuation of a widely

velocity-distributed argon atom beam through a C_{60} vapor is measured as a function of the time of flight.

V. CONCLUSION

A rigorous method has been used to determine the nonlocal response of a bubble made of a linear continuous medium, to the presence of a ground-state atom located inside as well as outside the bubble. General analytical expressions of inner and outer reflection factors $\Delta_i^{i,0}$ are obtained. Within the framework of the approximations used here, which are valid at intermediate distances, these factors contain all the physics of the problem, allowing us to calculate, by use of the propagator method, various quantities such as the polarization, the energy of interaction, etc. For sake of clarity only dipolar sources and dipolar propagators have been considered here, but the treatment (using the same factors $\Delta_i^{i,0}$) can be easily extended to higher orders. We have verified that when a local form of the response is assumed, then the general formula gives as a special case the reflection factors of a dielectric medium.

In the numerical calculations, more or less sophisticated models describing the atom and the medium properties can be used. In the case of a metal, the Jellium model, i.e., a gas of independent electrons confined within infinite potential barriers, is the simplest one able to account for the nonlocality of the response. This model can be improved, e.g., by introducing electronic correlation and exchange effects by means of the density-functional formalism.²⁶ Similarly more elaborated descriptions of the atomic or molecular polarizabilities and of the local properties of dielectric media can be introduced within the framework of the general theory.

Limiting geometrical configurations have been examined, allowing us to recover previous results obtained in simpler situations (spherical cavity, filled spheroid) or providing us

with new results (plate). Obviously at short distances between the atom and the solid, the description using a continuous medium becomes questionable and repulsive forces need to be considered. As it has been shown previously,¹ both features can be incorporated in the treatment by simply adding to the van der Waals energy a discrete sum over the solid lattice of the repulsive part of a 6–12 Lenard-Jones potential.

Applying the propagator method to the Ar-C system and then adding at short distances a sum of repulsive terms to the van der Waals energy, we have shown that the scattering of Argon atoms by fullerene molecules at subthermal and thermal energies leads to rather high differential cross sections, exhibiting easily observable rainbow features. Similarly the elastic total cross section, which exhibit a glory oscillation, should be also easily measured in a beam-gas time-of-flight experiment.

Other problems involving molecules instead of atoms can be treated by the same method. For example the dynamics of a polar or nonpolar diatomic molecule encapsulated inside a microsized bubble, a system equivalent to a triatomic molecule, is of a particular interest insofar as the anisotropic molecule-solid interaction couples the different degrees of freedom, which could lead to a very special rovibrational spectroscopy.

The extension to the cylindrical symmetry (an atom inside a nanotube) is feasible. It should extend the domain of applicability of the method to a wider variety of experimentally accessible systems.

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