

The polarizability of a confined atomic system: An application of Dalgarno-Lewis method

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Abstract. In this paper we give an application of Dalgarno-Lewis method, the latter not usually taught in quantum mechanics courses. This is very unfortunate since this method allows to bypass the sum over states appearing in the usual perturbation theory. In this context, and as an example, we study the effect of an external field, both static and frequency dependent, on a model-atom at fixed distance from a substrate. This can happen, for instance, when some organic molecule binds from one side to the substrate and from the other side to an atom or any other polarizable system. We model the polarizable atom by a short range potential, a Dirac- δ and find that the existence of a bound state depends on the ratio of the effective “nuclear charge” to the distance of the atom to the substrate. Using an asymptotic analysis, previously developed in the context of a single δ -function potential in an infinite medium, we determine the ionization rate and the Stark shift of our system. Using Dalgarno-Lewis theory we find an exact expression for the static and dynamic polarizabilities of our system valid to all distances. We show that the polarizability is extremely sensitive to the distance to the substrate creating the possibility of using this quantity as a nanometric ruler. Furthermore, the line shape of the dynamic polarizability is also extremely sensitive to the distance to the substrate, thus providing another route to measure nanometric distances. The ditactic value of the δ -function potential is well accepted in teaching activities due to its simplicity, while keeping the essential ingredients of a given problem.

1. Introduction

It is well known that the electric and optical properties of atomic systems are influenced by the presence of interfaces as discussed [Cahen *et al.*(2005)Cahen, Kahn, and Umbach]. In particular, the response to an electric field, characterized by shifts of the atom (or molecule) energy levels, known as the Stark shift, is no exception as shown in [Flatté *et al.*(2008)Flatté, Kornyshev, and Urbakh]. The Stark shift is often presented in a second course in quantum mechanics in the context of perturbation theory, however, this discussion seldom comes with an emphasis on a very common problem in perturbative calculations, which is the need to sum over an infinite number (or even a continuum) of states to evaluate the second order correction. This problem is exacerbated when a non-trivial geometry is considered, such as the mentioned proximity of the atomic system to an interface. In addition to the Stark shift, the energy levels, which are bound states in the absence of the applied field, become resonances and an ionization rate can also be defined from a complex energy eigenvalue. Physically, the electrons escape from the atom or molecule by tunneling through the finite barrier created by the applied electric field. It is often of interest to evaluate the electric response of such atomic or molecular systems as a function of distance to the interface. For instance, there exist relevant applications in biophysics related to the detection of organic molecules utilizing methods of Surface-Enhanced Raman Spectroscopy (SERS), discussed in [Braun *et al.*(2007)Braun, Lee, Dante, Nguyen, Moskovits, and Reich, Sabanayagam and Lakowicz(2006)], as well as other methods of probing their binding configuration, for instance those described in [Berlanga *et al.*(2017)Berlanga, Etcheverry-Berríos, Mella, Jullian, Gomez]. The Raman-effect, in particular, can be strongly enhanced by attaching artificial atoms to one end of organic chains. In such a system, organic molecules will bind to a dielectric substrate at the one end and to an atomic system or quantum dot at the other, as illustrated in Fig. 1. In the same figure, we also illustrate the use of the static polarizability to measure the number of deposited atomic layers on a substrate (right part of the figure).

Varying the distance a (see Fig. 1) leads to significant changes in the dynamic polarizability of the atomic system and, consequently, to the optical scattering cross section of electromagnetic radiation (which is proportional to the imaginary part of the dynamic polarizability as discussed in [van de Hulst(1958), van de Hulst(1981)]). These changes to the polarizability, in turn, may result in the creation of electromagnetic hot-spots which result in the amplification of the Raman-scattering signal of the organic molecules.

We also note that there exists, as will be argued in the next sections, a strong dependence of the static polarizability on a . We are, thus, driven to suggest that measurements of the static polarizability of such a system may act as a kind of nanometric ruler which allows for the determination of the thickness of atomic layers. To quantitatively describe the dependence of the polarizability on a , we consider a simple 1D model for an hydrogen-like atom. The model consists of a short range interaction given by a δ -function to represent the atomic system. The δ -function is often used as a toy-model for atomic systems since it manages to keep the mathematical complexity at a relative minimum while still providing insight into their qualitative and quantitative behavior. For instance, in the classic textbook by Cohen-Tannoudji *et al.* [Cohen-Tannoudji *et al.*(1977)Cohen-Tannoudji, Diu, and Laloe], an example of two δ -functions being used to model a molecule is explored

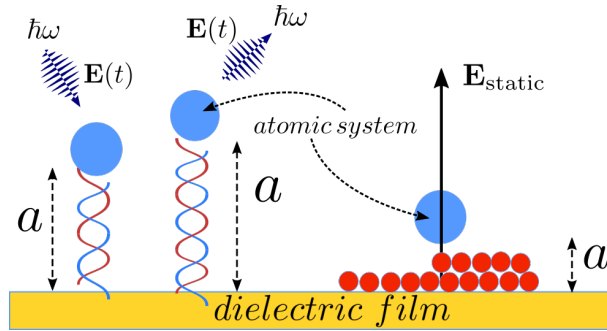


Figure 1. Schematic illustration of organic chains with length a bound to an atomic system (blue dots) at one end and to a dielectric substrate at the other. The length of the organic chain allows for the control of the distance of the atomic system to the dielectric substrate. When an external frequency-dependent electric field is applied to the system, the dynamic polarizability can be modified by changing the organic molecule length, which results in the creation of electromagnetic hot-spots and therefore in the enhancement of Raman-scattering signals, allowing for detection. In addition, for smaller distances (see right hand side of the figure with one and two layers of atoms (red dots) separating the atomic system from the substrate), as will be argued in the following sections, the static polarizability depends very sensitively on the distance a , and as such, by measuring this polarizability, one can obtain information about the number of atomic layers separating the atomic system from the substrate. This system can thus be used as a nanometric ruler.

and manages to capture the essential aspects of the bonds formed between atoms. Nevertheless, this simplified approach has been shown to provide accurate results in the prediction of the electrical properties of 3D H_2^+ molecules in [Henriques *et al.*(2021)Henriques, Pedersen, and Peres], despite being of considerably more simplicity than the full Coulomb problem.

In the particular case of the system we are considering, this approach has the advantage of allowing analytic solutions to the quantities relevant to our calculations, such as the static and dynamic polarizability of the atomic system, which makes it a pedagogically valuable model for introducing perturbative calculations and keeping the focus away from potential mathematical or numerical details of the description of the unperturbed system.

In our study, we will use asymptotic methods for obtaining the ionization rate and Stark shift as well as the polarizability when such a system is subjected to an external and static electric field. This procedure, developed in [Fernandez and Castro(1985)] relies on the asymptotic expansions of the Airy functions (other methods exist, such that developed in [Geltman(2001)]). These are exact solutions to the Schrödinger equation in the presence of a static electric field and allows for expressions to be found for both ionization rate and Stark shift when the distance from the atomic system to the substrate is small. Emphasis will be given, however, to the method developed in [Dalgarno and Lewis(1955), Karplus(1962), Karplus and Kolker(1963), Mossman *et al.*(2016)Mossman, Lytel, and Kuzyk] which is useful in replacing sums over an infinite number of states, often impossible to calculate directly, by the solution of an inhomogeneous differential equation. This method allows us to provide an analytic expression for the static polarizability of the atomic system as a function of distance to the surface for an arbitrarily large or small value of this quantity.

In addition, we provide a means of calculating the dynamic polarizability, which characterizes the response of the atomic system to a frequency-dependent electric field using a method developed in [Fowler(1984)]. This method is a very natural extension of Dalgarno-Lewis theory to time and frequency dependent perturbations. This stress the didactic value of the method for tackling time-dependent problems.

We would like to remark, yet again, that the method of Dalgarno-Lewis is very powerful for bypassing the sum over states appearing in the usual perturbation theory. This makes it a valuable tool when going beyond the simplest examples discussed in quantum mechanics courses where this sum is solvable analytically or often reduced to a few terms. This paper presents an application of this method in the context of a relatively simple quantum-mechanical model which has a certain degree of physical relevance as pointed out above. The basic model is a simple problem in quantum mechanics, but the application of an ac field or a dc field makes this problem non-trivial. We believe that the problem we tackle in this paper has a high pedagogical value for advanced undergraduate students in quantum mechanics or students starting their graduate studies, as well as managing to provide insight into the physics that underlie the model.

This paper is organized as follows: in Sec. 2 we introduce our model and give the asymptotic solution of the complex eigenvalue problem. In Sec. 3 we provide the exact solution to both the static and the dynamic polarizabilities of our system, using Dalgarno-Lewis' method. In Sec. 4 we provide our conclusions. The paper ends with an appendix on the solution of the inhomogeneous differential equation.

2. The ionization rate using Fernández's method

In this section we introduce our model and obtain the condition for the existence of a bound state. Later, using asymptotic methods we derive the ionization rate and the Stark shift for our system when subjected to an external and static electric field.

2.1. Model and condition for the existence of a bound state

We are interested in obtaining the shift in energy levels as well as ionization rate of an atomic system in proximity to a substrate. The problem, therefore, amounts to solving a Schrödinger equation with total potential energy given by the sum of the attractive nuclear potential close to a substrate and the perturbation caused by a static electric field. We note, however, that the solution of the Schrödinger equation with Hamiltonian given by the Coulomb potential is cumbersome, if not impossible for this geometry. As such, we use a very simple model consisting of a single attractive δ -function potential energy. It has been noted before in the literature, that the delta function is a good one-dimensional model for the three dimensional atom with the full Coulomb interaction. This similarity arises from the fact that both potentials are singular at the origin as well as behaving in a similar fashion under derivatives, that is we have that $\delta'(x) = -\delta(x)/x$ and $\nabla 1/r = -1/r^2$, which corresponds to the same functional relation for both potentials and implies the same form of the virial equation (see [Fernandez and Castro(1985), Henriques *et al.*(2021)Henriques, Pedersen, and Peres]). This potential therefore allows us to keep the mathematics relatively simple, while capturing the essential physical features of our system. For this reason, the δ -function model is useful for obtaining a rough insight into the physics atomic-line systems and can often be used

as a first introduction to atomic and molecular dynamics in an introductory quantum mechanics course. We shall see that the solution to the Schrödinger equation for our system in the absence of the applied electric field is straightforward. Written in atomic units, such that $\hbar = e = m = 1$, the Schrodinger equation is given by

$$\left(-\frac{1}{2}\frac{d^2}{dx^2} - Z\delta(x) - \varepsilon_b\right)u_b(x) = 0. \quad (1)$$

The solution of the Schrödinger equation will then give the bound state wave-function u_b with bound state energy ε_b . The parameter Z represents an effective nuclear charge. The presence of the substrate at a distance $x = -a$ imposes a boundary condition for the wave function such that $u_b(-a) = 0$. Since we are interested in bound states, we consider only states with negative energy, written as $\varepsilon_b = -k_b^2/2$. For $x \neq 0$ the solution to the equation is given as a linear combination of exponentials with positive and negative arguments. As such, to fulfill the boundary condition at $x = -a$ and to obtain a normalizable wave function we must have an evanescent wave for $x > 0$ and a hyperbolic sine for $-a < x < 0$. The coefficients can be obtained imposing the continuity of the wave function at $x = 0$. This gives the full solution of the bound state wave-function

$$u_b(x) = \begin{cases} 0 & x < -a, \\ 2Ae^{-k_b a} \sinh(k_b(x+a)) & -a < x < 0, \\ 2Ae^{-k_b a} \sinh(k_b a) e^{-k_b x} & x > 0. \end{cases} \quad (2)$$

Here, the normalization coefficient is given by the radical $A = \sqrt{k_b/(1 - e^{-2k_b a}(1 + 2k_b a))}$. For further physical insight into the shape and behavior of the wave function, we plot it, along with the potential in Fig. 2 .

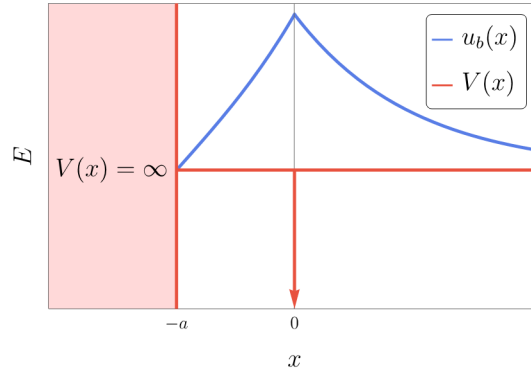


Figure 2. Illustration of atomic model potential $V(x)$ (red) and bound state wave function $u_b(x)$ (blue) obtained by the described procedure. The region coloured in light red corresponds to the substrate which we model by an impenetrable surface with an infinite potential. The remaining part of the potential corresponds to the short range Dirac- δ which goes to $-\infty$ at $x = 0$ and is zero otherwise. The wave function is a hyperbolic sine for $0 < x < -a$, and a decaying exponential for $x > 0$.

To obtain the bound state energy we look at the discontinuity of the derivative of the wave function characteristic of delta-function potentials $u_b'(0^+) - u_b'(0^-) = -2Zu_b(0)$. This allows us to calculate the “wave vector” k_b as the solution to a transcendental equation, which can be easily be obtained numerically, and reads

$$\frac{k_b}{Z} = 1 - e^{-2k_b a}. \quad (3)$$

We note that as the distance from the model atom to the barrier goes to zero, we obtain $1/Z = 2a(1 + k_b a)$. This equation can only have a solution if $Z > 1/2a$. Therefore we have a limiting condition for the existence of a bound state in our problem. Note that for the isolated model atom, where the wave-function spreads over the whole space, any finite value of Z leads to a bound state.

2.2. Asymptotic solution of the resonant problem

We now obtain, through the asymptotic method outlined in the paper of Fernandez and Castro [Fernandez and Castro(1985)] an expression for both the ionization rate and the Stark shift of our model atom. Applying an external and static electric field to the system, the Schrödinger equation with Hamiltonian given in the dipole approximation, becomes

$$\left(-\frac{1}{2} \frac{d^2}{dx^2} - Z\delta(x) - \varepsilon - Fx \right) \psi_\varepsilon(x) = 0. \quad (4)$$

For $F > 0$, the strength of the electric field, and $x \neq 0$ this equation can be written in a more convenient form under the change of variables $y = (2/F^2)^{1/3} (Fx + \varepsilon)$. It then becomes the Airy equation with solutions given by the Airy functions $Ai(-y)$ and $Bi(-y)$. These functions oscillate for $y > 0$ and are exponentially decaying or growing functions for $y < 0$, in the case of $Ai(-y)$ and $Bi(-y)$, respectively. This corresponds, as expected, to a quasi-bound state brought on by the deformation of the potential caused by the application of the electric field. In other words, the application of a static field results in the previously bound electron having a probability of undergoing tunneling ionization. Fortunately, a general solution to this Airy equation exists and is given by

$$\{ a Ai(-y[x]) + b Bi(-y[x]) - a < x < 0, c Ai(-y[x]) + d Bi(-y[x]) x > 0, \quad (5)$$

where a, b, c , and d are constant coefficients needed to be determined.

The wave function that solves equation (4) will be a sum of both Airy functions for $-a < x < 0$ in such a way that the boundary condition for the impenetrable barrier will still be obeyed. If we define $\beta = y(-a)$ we have that $b = -a Ai(-\beta)/Bi(-\beta)$. We can also impose that the wave-function have an asymptotic form corresponding to a traveling wave propagating outwards from the origin. To impose such a condition we look at the asymptotic form of the Airy functions as $y \rightarrow \infty$:

$$Ai(-y) = \pi^{-1/2} y^{-1/4} \sin \left(\frac{2}{3} (-y)^{3/2} + \frac{\pi}{4} \right), \quad (6)$$

$$Bi(-y) = \pi^{-1/2} y^{-1/4} \cos \left(\frac{2}{3} (-y)^{3/2} + \frac{\pi}{4} \right). \quad (7)$$

This leads to the choice of coefficients $c = id$, made in keeping with the idea that the wave-function should look like an outgoing wave, or in this case, like $Ci(-y) = Bi(-y) + iAi(-y)$. We now can turn our attention to the boundary conditions at $y = 0$. These are given by a system of equations consisting of the continuity of the wave function and discontinuity of its derivative. Defining $\alpha = y(0)$, $\gamma = Bi(-\beta)/Ai(-\beta)$ we can write boundary conditions as

$$a(\gamma Ai(-\alpha) - Bi(-\alpha)) + c Ci(-\alpha) = 0 \quad (8)$$

$$\begin{aligned} & a(2F)^{1/3} (Bi'(-\alpha) - \gamma Ai'(-\alpha)) \\ & + 2ZcCi(-\alpha) - (2F)^{1/3} Ci'(-\alpha) = 0. \end{aligned} \quad (9)$$

We can view the previous system as a product of a 2×2 matrix with a vector of coefficients a and c being equal to the zero vector. For such a system to have non-trivial coefficients a and c and, thus, a non-trivial wave-function we must have that the determinant of the matrix be zero. This condition can be written explicitly as

$$\begin{aligned} & (2Z\pi)Ci(-\alpha)(Ai(-\alpha)Bi(-\beta) \\ & - Bi(-\alpha)Ai(-\beta)) - (2F)^{1/3}Ci(-\beta) = 0, \end{aligned} \quad (10)$$

where we have use the Wronskian of the Airy functions, which reads $Ai'(-\alpha)Bi(-\alpha) - Bi'(-\alpha)Ai(-\alpha) = 1/\pi$. We will now use this result to obtain an asymptotic result for both the Stark shift and the ionization rate. We start by noting that both α and β go to negative infinity in the weak field limit $F \ll 1$. As such, we may replace in equation (10) the asymptotic expressions for the Airy functions when their arguments go to positive infinity (see Ref. [Abramowitz and Stegun(1964)]).

$$Ai(y) = \frac{1}{2}\pi^{-1/2}y^{-1/4}e^{-\zeta} \sum_{i=0}^{\infty} (-1)^i c_i \zeta^{-i}, \quad (11)$$

$$Bi(y) = \pi^{-1/2}y^{-1/4}e^{\zeta} \sum_{i=0}^{\infty} c_i \zeta^{-i}, \quad (12)$$

where $\zeta = 2y^{3/2}/3$, $c_0 = 1$ and $c_k = \frac{\Gamma(3k+1/2)}{(54^k k! \Gamma(k+1/2))}$.

Setting both real and imaginary parts equal to zero we may obtain expressions for the real and imaginary parts of the wave vector k . We may notice then, that the imaginary part is small when compared to the real part, as it can be shown to depend on $e^{-2\zeta}$. For all intents and purposes, this allow us to write $k \approx Re(k)$. We may calculate the real part of k , for which only the lowest order terms in F in both series of the Airy functions are considered. Expanding this in powers of a and equating the result with k itself, and yet again retaining only the lowest order terms, we may obtain a polynomial equation for k which depends on F . Solving this polynomial equation allows us to write an asymptotic expression for $Re(k)$ in the limit $F \ll 1$, $a \ll 1$ as a power series of F . If we write the power series of the energy using $\varepsilon = -k^2/2$, the zeroth order term in F is simply given by the bound state energy $\varepsilon_b = -k_b^2/2$ and the second order term of this series corresponds to the Stark shift in the weak field and small distance limit. Thus we can write the Stark shift $\Delta\varepsilon^{(2)}$ as:

$$\Delta\varepsilon^{(2)} = -\frac{5F^2}{8k_b^4} \quad (13)$$

We can then substitute the bound state energy considering only a zeroth order approximation for k in the equation for $Im(k)$ and obtain the imaginary part of the energy. In atomic units the ionization rate is given by $\Gamma = -2Im(\varepsilon)$ and can, as a result of our calculations, be written as

$$\Gamma = \frac{k_b^3}{Z} e^{-\frac{2k_b^3}{3F}}. \quad (14)$$

The presence of F in the denominator of the exponential indicates that this result is non-perturbative but we note again that the results of equations (13) and (14) are only strictly true in the weak field and small distance limit, and as such, in the following sections we present an alternative exact method for calculating the Stark shift valid for all values of a and therefore characterize the response of the model atom to an applied electric fields through an exact calculation of the static polarizability.

3. Exact calculation of the static and dynamic polarizability

Usually, the direct approach to the calculation of a response function faces enormous difficulties due to the necessity of summing over all eigenstates of the system. Dalgarno and Lewis [Dalgarno and Lewis(1955)] circumvented this difficulty reducing the need of summing over all states to the solution of an inhomogeneous differential equation. In this section we obtain the exact expression to the static polarizability of our model-atom using the Dalgarno-Lewis approach. This same approach is possible in the case of a frequency dependent electric field using a method due to Fowler [Fowler(1984)]. The Dalgarno-Lewis method (and its generalization to time-dependent problems performed in [Karplus(1962), Karplus and Kolker(1963)]) has been applied to many different problems, relevant examples being the effect of phonons on the ground state of a Wannier exciton discussed in [de Vooght and Bajaj(1973)]; the effect of confinement on the Stark effect analyzed by Pedersen [Pedersen(2017)]; the study of nonlinear optics considered in [Thayyullathil *et al.*(2003)Thayyullathil, Radhakrishnan, and Seema, Radhakrishnan and Thayyullathil(2004)]; and the list goes on, including particle physics and astrophysics. We believe that this method may also be useful for students first learning about perturbation theory methods, as its discussion not only shines a spotlight on the difficulty of evaluating infinite sums over states, but also, provides an easily graspable and elegant workaround to this problem. Here we use the method to compute both the static and the dynamic polarizability of our semi-confined system as an illustration of its usefulness as well as a means of capturing the physics of the simple model we proposed.

3.1. The Dalgarno-Lewis method revisited

The Dalgarno-Lewis perturbation theory is seldom discussed in text books on quantum mechanics. This is very unfortunate since the method is very powerful for summing an infinite number of states (a task that cannot, in general, be done by a direct brute-force approach). Some notable exceptions which do cover Dalgarno-Lewis theory are the books of Desai [Desai(2009)] which uses the method to calculate the polarizability of an Hydrogen atom, as well as Refs. [Konishi and Paffuti(2009)] and [Schiff(2010)] which provide a pedagogical account of the theory. Therefore, we give here a brief, but enough detailed, derivation of Dalgarno-Lewis perturbation theory, using Dirac notation for generality and following the approach of Schiff [Schiff(2010)] . Some knowledge of Rayleigh-Schrodinger (RS) perturbation theory is assumed for this section, such as the form of the second order correction to the energy, or the first order correction to the wave-function, but accounts of these topics can be found in most classic textbooks on quantum mechanics. However, we note that there exist approaches to the derivation of Dalgarno-Lewis theory that do not rely so much on usual RS perturbation theory, such as that developed in

[Balantekin and Malkus(2010)] for algebraic Hamiltonians.

It is a well known result from RS perturbation theory that if a Hamiltonian can be written in the form $H = H_0 + H'$, where H' is a perturbation that is small compared to H_0 , then the second order correction to the energy for a non-degenerate state (in particular the ground-state of a one dimensional system, which is always non-degenerate) is given by

$$\Delta\varepsilon^{(2)} = \sum_{n \neq m} \frac{\langle m | H' | n \rangle \langle n | H' | m \rangle}{E_m - E_n} \quad (15)$$

where the sum runs over both the remaining bound states and the whole continuum of scattering states. In the case that the states form a continuum, this is to be replaced by an integral. The Dalgarno-Lewis method starts by assuming that there exists an operator O such that

$$\frac{\langle n | H' | 0 \rangle}{E_0 - E_n} = \langle n | O | 0 \rangle. \quad (16)$$

This might seem, at first, like a large leap or arbitrary choice, but we shall see that the operator O has a precise physical meaning. Writing the second order correction to the energy using the operator O we have

$$\begin{aligned} \Delta\varepsilon^{(2)} &= \sum_{n \neq 0} \langle 0 | H' | n \rangle \langle n | O | 0 \rangle \\ &= \langle 0 | H' \sum_{n \neq 0} | n \rangle \langle n | O | 0 \rangle \end{aligned} \quad (17)$$

The sum of $|n\rangle \langle n|$ over the whole Hilbert space is a partition of the identity and, since in equation (17) the sum runs over all but the ground state, we may write

$$\Delta\varepsilon^{(2)} = \langle 0 | H' O | 0 \rangle - \langle 0 | H' | 0 \rangle \langle 0 | O | 0 \rangle. \quad (18)$$

We have thus avoided the integral over states. We have only to rewrite this equation in such a way as to bring out the dependence in the first order correction to the wave-function. To do this we make use of the definition of O and are able to write $\langle n | H' | 0 \rangle$ as $\langle n | [O, H_0] | 0 \rangle$ where $[\cdot, \cdot]$ is the commutator. This can be easily checked by simply letting O act on $|0\rangle$ and then rewriting the energy eigenvalues as the operator H_0 acting on the respective states:

$$\begin{aligned} \langle n | H' | 0 \rangle &= \langle n | O (E_0 - E_n) | 0 \rangle \\ &= \langle n | -H_0 O + O H_0 | 0 \rangle \\ &= \langle n | [O, H_0] | 0 \rangle \end{aligned} \quad (19)$$

This equality however can be written as an equality between operators up to a constant $[O, H_0] = H' + C$. The equality holds for an arbitrary choice of C , since, by non-degenerate perturbation theory, the sum occurs over $n \neq 0$ and the states are orthogonal, from which it is clear that $\langle n | C | 0 \rangle = C \langle n | 0 \rangle = 0$. In particular, taking $n = 0$, we can now say that

$$\langle 0 | [O, H_0] | 0 \rangle = \langle 0 | H' | 0 \rangle + C. \quad (20)$$

We now take advantage of the freedom in the choice of C . Since it must be true that $\langle 0|[O, H_0]|0\rangle = 0$ we then have that $C = -\langle 0|H'|0\rangle$. If we now define $|\psi_1\rangle = O|0\rangle$ we may write

$$(E_0 - H_0)|\psi_1\rangle = H'|0\rangle - \langle 0|H'|0\rangle|0\rangle. \quad (21)$$

From Rayleigh-Schrödinger Perturbation theory it is easy to show that $|\psi_1\rangle$ corresponds, by definition of the operator O , to the first order correction to the wave function. We have only to multiply on the left and right hand sides of equation 16, by $|n\rangle$ and then sum over $n \neq 0$. Using the partition of the identity, we are left with the usual expression for the first-order correction:

$$\begin{aligned} \sum_{n \neq 0} \frac{\langle n|H'|0\rangle}{E_0 - E_n} |n\rangle &= \sum_{n \neq 0} (|n\rangle \langle n|) |\psi_1\rangle \\ \Leftrightarrow |\psi_1\rangle &= \sum_{n \neq 0} \frac{\langle n|H'|0\rangle}{E_0 - E_n} |n\rangle. \end{aligned} \quad (22)$$

We now see that the operator O gives the first order correction to the wave-function when acting on the ground state, and can be regarded as the first term $O_{0,1}$ in a series $S_n = \sum_i O_{n,i}$ that gives the eigenstates of the full Hamiltonian H from the eigenstates $|n\rangle$ of the unperturbed Hamiltonian H_0 by generating the successive corrections (see Ref. [Balantekin and Malkus(2010)]).

From these considerations, we can see that the Dalgarno-Lewis procedure amounts to substituting the sum over states of equation (15 or 22) with the solution of the inhomogeneous differential equation (21), referred to as the Dalgarno-Lewis equation. This solution gives us the first order correction to the wave function, while from usual perturbation theory, the correction to the energy is evaluated as

$$\Delta\varepsilon^{(2)} = \langle 0|H'|\psi_1\rangle. \quad (23)$$

In the rest of the paper, this method will be applied in the next section to the calculation of the Stark shift and static polarizability of the model-atom.

3.2. Application to the calculation of the static electric polarizability

The static polarizability is a response function of a system to a static electric field. For non-degenerate ground states the linear order polarizability is zero. The second order polarizability, however, is finite and it will concern us in this section. Let us apply the formalism introduced in the previous subsection, now adapted to a problem written in real space. Our bound state $|0\rangle$ corresponds to the bound state wave function given in equation (2), the zeroth order Hamiltonian H_0 will have the potential included in equation (1) and the perturbation Hamiltonian H' is given by the term of equation (4) that depends on the electric field intensity $-Fx$. The Dalgarno-Lewis equation reads, in real space

$$\begin{aligned} &\left(-\frac{k_b^2}{2} + \frac{1}{2} \frac{d^2}{dx^2} + Z\delta(x)\right) \psi_1(x) \\ &= \left(-Fx - \int_{-a}^{\infty} dx (-Fxu_b^2(x))\right) u_b(x). \end{aligned} \quad (24)$$

Both the integral and the resulting differential equation can be solved as shown in the Appendix. The correction to the wave function is obtained as explained in the Appendix, and the integral entering in equation (24) can be readily computed yielding

$$\Delta\varepsilon^{(2)} = \frac{(-2a(2a^2k_b^2 - 15)(Z - k_b) - 15)}{24k_b^4(2a(k_b - Z) + 1)} F^2. \quad (25)$$

This result is, in contrast to those presented in Eq. (13), valid for all values of strength of the atom potential Z as well as the distance a . In particular, when $a \ll 1$ if we retain only powers of zero order of a we recover the asymptotic result previously derived for the Stark shift.

We now turn our attention to an interpretation of the Stark shift as a measure of the second order static polarizability, which corresponds to an induced dipole moment measured by the static polarizability α . The polarizability is itself defined through

$$\Delta\varepsilon^{(2)} = -\frac{1}{2}\alpha F^2. \quad (26)$$

Thus, from equation (25) we can see that the static polarizability is given by

$$\alpha = \frac{(2a(2a^2k_b^2 - 15)(Z - k_b) + 15)}{12k_b^4(2a(k_b - Z) + 1)}. \quad (27)$$

If we hold Z fixed as a parameter of our atomic model, we may vary the distance a and see how this affects the static polarizability. Note that k_b will also change as a consequence of the transcendental equation (3). The polarizability will increase dramatically as a result of the presence of the substrate located at $x = -a$ as can be seen in Fig. 3 in blue, and will otherwise tend to a finite value corresponding to the static polarizability of the isolated atomic system as the distance from substrate becomes large. From Fig. 3 we notice a strong deviation from the isolated atom polarizability for values of a smaller than 10 a.u.=0.5 nm. Considering that the size of a carbon atom is about 0.22 nm, the change in the static polarizability will be sensitive to differences in one layer to two layers of atoms separating the atomic system from the substrate, as depicted in Fig. 1.

3.3. Calculation of the dynamic polarizability

In this section we concern ourselves with the application of an external time and frequency dependent electric field and therefore study the optical response of the system, thus showing that the Dalgarno-Lewis method can also be applied to time-dependent problems. This amounts to considering an applied electric field of the form $F(t) = -F(e^{i\omega t} + e^{-i\omega t})$ and solving the time dependent Schrodinger equation:

$$i\frac{\partial}{\partial t}\psi_\varepsilon(x, t) = [H_0 + F(t)x]\psi_\varepsilon(x, t), \quad (28)$$

where H_0 is the Hamiltonian of the atomic system in proximity to the substrate. Following the approach of Fowler we consider a time dependent perturbation such that:

$$\begin{aligned} \psi_\varepsilon(x, t) \approx & u_b(x)e^{ik_b^2t/2} + \phi_1^+(t)e^{i(k_b^2/2+\omega)t} \\ & + \phi_1^-(t)e^{i(k_b^2/2-\omega)t}. \end{aligned} \quad (29)$$

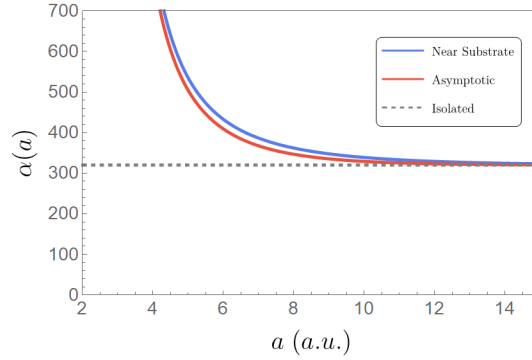


Figure 3. Plot of the static polarizability of the isolated model-atom (dashed and gray) and model-atom in the vicinity of a substrate (blue). We compare the results with the asymptotic calculation given in equation (13) (red). Here we have chosen the effective nuclear charge $Z = 0.25$ and plot the polarizability as a function of distance from the substrate, a , in atomic units (a.u.). Note that in our atomic system modeled by a δ -function potential, there is no *a priori* restriction that Z be whole and thus can take values smaller than 1. As can be seen, the presence of the substrate causes an extremely sharp increase in polarizability for small distances, which are close to the limiting condition $a = 1/(2Z)$ obtained from equation (3). As is expected, for larger distances, the effects of the presence of the substrate are much smaller and both polarizabilities coincide for large a . The value $Z = 0.25$ is chosen so that there occurs significant deviation from the polarizability of the isolated atom for a at the scales below 10 a.u. or, in S.I. units, at 0.5 nm.

Substituting equation (29) into equation (28) and grouping terms in the same exponentials we further obtain a differential equation for ϕ_1^\pm of the form:

$$\left[-\frac{1}{2} \frac{\partial^2}{\partial x^2} - Z\delta(x) + \left(\frac{k_b^2}{2} \pm \omega \right) \right] \phi_1^\pm(x) = Fx u_b(x). \quad (30)$$

As before, we are able to determine the first order correction to the wave-function, as well as the Stark-shift through the use of equation (23) and which now takes the form

$$\alpha(\omega) = \frac{2}{F^2} \left[\langle b | Fx | 1 \rangle^+ + \langle b | Fx | 1 \rangle^- \right]. \quad (31)$$

Where $\langle x | 1 \rangle^\pm = \phi_1^\pm(x)$. This allows us to obtain an analytic expression for the dynamic polarizability of the model-atom through the use of equation (26), which we omit due to it being extremely cumbersome. In essence, this approach is very similar to the Dalgarno-Lewis method in the sense that an infinite sum over states is also avoided through the solution of an inhomogeneous differential equation, however a dependence on the frequency comes into play, which as seen in Fig. 4 and 5 plays an important role in the physical description of the system.

In Fig. 4 we see that despite the fact that the imaginary part of the dynamic polarizability is nonmonotonic in a , the size of its peaks become larger as a becomes smaller. We therefore are able to conclude that, electromagnetic hot-spots can occur when the system is subjected to a frequency-dependent electric field even for large distances to a substrate, but in particular, these effects are greatly exacerbated for small distances to the substrate. More importantly, the shape of the curves of the

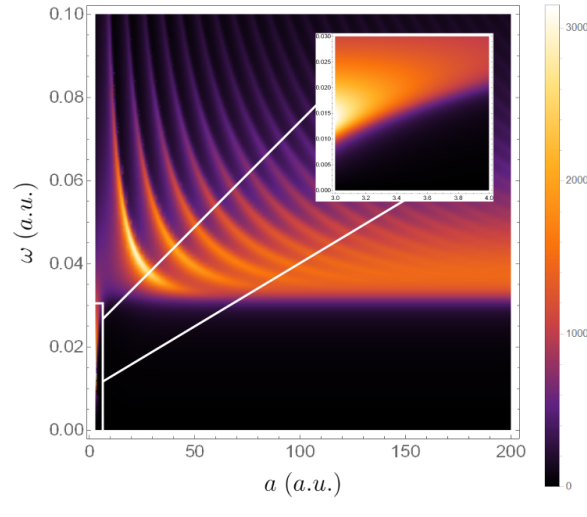


Figure 4. Plot of the imaginary part of the dynamic polarizability of the atomic system near a substrate. Here we have chosen the effective nuclear charge $Z = 0.25$ and plot the polarizability as a function of distance from the substrate and frequency in atomic units. Firstly we note that there exist peaks of greater polarizability in the vicinity of the substrate. We also find that there exists a very sharp increase of polarizability for small frequency and small distance (see zoomed in portion) as is necessary for the dynamic polarizability to match the static case as $\omega \rightarrow 0$. For large distances the peaks and troughs of polarizability meld together and converge to the result of the isolated atom visible on the bottom right as a continuous slope. Note that a small imaginary part was added to the frequency for the results to be finite (the value of the imaginary part used is $0.0018 \text{ a.u.} = 50 \text{ meV}$). This is necessary as it accounts for a broadening of the energy levels of the atomic system caused by the existence of a decay rate associated with ionization.

polarizability as function of frequency are considerably different for different distances of the atomic system to the substrate. Therefore, scanning the system in frequency and retrieving its dynamic polarizability gives a measure of the distance of the atomic system to the substrate or, in the context of probing a deposit on the substrate, a measure of the number of molecular layers in between the substrate and atomic system. The discrimination of the distance can extend up to $a = 50 \text{ a.u.}$. We also note the existence of strong oscillations in the imaginary part of $\alpha(\omega)$ for large values of a . These are due to interference effects brought by the presence of the impenetrable substrate, originated on the scattering states.

4. Conclusion and outlook

In this paper we have studied several aspects of the electrical and optical response of a one dimensional atomic system consisting of a δ -function when close to a substrate and subjected to an external and static as well as a frequency-dependent electric field. This was done in the context of providing a simple and physically relevant example of the application of the Dalgarno-Lewis method in perturbation theory. We started by giving a limiting condition for the existence of a bound state and obtaining a transcendental equation that allows for the calculation of the bound

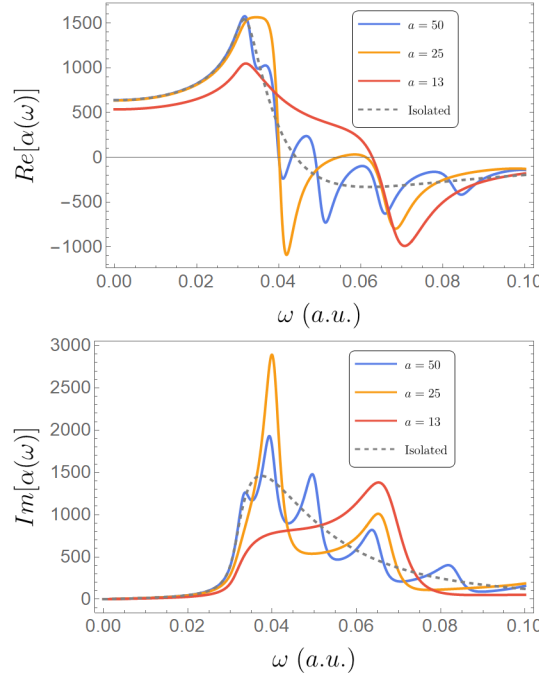


Figure 5. Plot of the real and imaginary parts of the dynamic polarizability of the atomic system with $Z = 0.25$ as a function of frequency of the applied field for several values of distance a (blue, orange and red). These curves can be understood as vertical cuts of Fig. 4. We also plot the dynamic polarizability of the isolated atom (gray and dashed) as a reference for the effects of the presence of the substrate. From the plots we see that decreasing a results in an increase in the size of the resonances of the polarizability, but also a decrease in the number of these resonances. Further increasing the distance will cause the peaks to occur with a much higher frequency but be smaller in size and the curve of the polarizability will eventually be indistinguishable from that of the isolated atom. This is also visible in Fig. 4. As in the latter, a small imaginary part (0.0018 a.u.=50 meV) was added to the frequency for the imaginary part of polarizability to be finite.

state energy as a function of distance and of the effective nuclear charge of our toy-model. We then provided asymptotic results for the ionization rate and Stark shift using asymptotic expansions of the Airy functions and the boundary conditions of our problem in order to write a condition for a non-vanishing wave function. The limit for small distances of such an expression allows for the calculation of a complex energy of which the real part corresponds to the Stark shift and imaginary part to the ionization rate. We have also provided a general derivation of the Dalgarno-Lewis method for perturbation theory, which we believe could be a welcome addition to many advanced undergraduates and early graduate students' tool-belts. The method allowed for a calculation of an exact second order correction to the energy for any distance to the substrate, which would otherwise be difficult for such a geometry. This result was seen to match the asymptotic one in the appropriate limit and allowed for a characterization of the static polarizability of our model-atom as a function of distance to the substrate, and unraveled some rich behavior within our simple model: The polarizability was seen to match the isolated atom for large distances, as expected,

but we showed that it increases quite dramatically when the atomic system is close to the substrate. Therefore, we argue that the measurement of the static polarizability of atomic systems can act as a “molecular ruler”, useful, for instance, in the context of the measurement of atomic distances to a substrate. An example can be the measurement of the thickness of atomic layers, deposited on a substrate. Through the calculation of the dynamic polarizability we have showed the existence of large resonances in the dynamic polarizability for small distances, which in the context of a substrate bound to DNA or other organic molecules, may result in an increased Raman-scattering signal from these molecules to which the atomic system is bound. This may therefore allow for an increased sensitivity in the detection of the presence of organic molecules bound to surfaces and covered by polarizable particles. The shape of the curve of the dynamic polarizability as a function of the applied electric field frequency was shown to be very sensitive to the distance to the substrate. As such we have argued that the change of the polarizability with the distance, which can be rather strong, can function as a nanometric ruler both in the static and dynamic cases and for small enough distances. For the parameters shown in the figures the strong enhancement occurs in the scale below 1 nm for the static polarizability but we may also consider the case of an atomic system with a smaller effective charge Z where the enhancement occurs at larger scales. In the case presented in the text, the system would indeed function as an atomic ruler, allowing to probe very thin layers of deposited molecules on a substrate. In particular, we can envision a strong interaction between the atomic system and the panoply of recently obtained two-dimensional (2D) materials. These systems, being essentially a surface are the perfect test bed of our ideas, since we would have both a very small distance between the 2D-materials and high sensitivity to small changes in the distance between the 2D-material and the atomic system.

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Appendix A. Solving the Dalgarno-Lewis Equation

We show, in this appendix, a few steps of the solution of the Dalgarno-Lewis equation (24). We start by solving the Integral

$$\int_{-a}^{\infty} dx Fx u_b(x) = 2Ae^{-k_b a} \int_{-a}^0 dx \sinh(k_b(x+a))$$

$$+ 2Ae^{-k_b a} \sinh(k_b a) \int_0^\infty dx e^{-k_b x}. \quad (\text{A.1})$$

By direct computation of both integrals we obtain a simple coefficient

$$\int_{-a}^\infty dx Fx u_b(x) = \frac{aF(Z - k_b)}{2a(Z - k_b) - 1}. \quad (\text{A.2})$$

Where we have also used the transcendental equation for k_b . This coefficient is merely a constant with respect to x which we will now call D . The Dalgarno-Lewis equation therefore becomes, by virtue of the piece-wise definition of the bound state wave-function, a piece-wise, second order inhomogeneous differential equation defined as

$$\psi_1''(x) - k_b^2 \psi_1(x) = 2(Fx - D)2Ae^{-k_b a} \times \sinh(k_b(x + a)), \quad -a < x < 0, \quad (\text{A.3})$$

$$\sinh(k_b a)e^{-k_b x}, \quad x > 0. \quad (\text{A.4})$$

Both parts of the equation consist of inhomogeneous differential equations where the term independent of $\psi_1(x)$ is either an exponential, a polynomial or at most a product of the two. There are many well known methods for solving such equations, and applying any of them yields a solution for $\psi_1(x)$. We omit here this function as its analytic representation is cumbersome and brings no practical insight despite consisting only of products of exponential functions and polynomials. The energy correction corresponding to the Stark shift requires the calculation of yet another integral corresponding to plugging in $\psi_1(x)$ as well as $-Fx$ into equation (23)

$$\Delta\varepsilon^{(2)} = -F \int_{-\infty}^\infty dx u_b(x)x\psi_1(x). \quad (\text{A.5})$$

This is yet again an integral of products of exponentials and polynomials and, as such, a computation of relative ease yields equation (25).

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