

An algebraic method to determine the local field of condensed system

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Abstract. An algebraic method is proposed to generate a self-consistent converged complex polarizability of atoms and molecules from limited available data. An iterative method is also suggested to generate the general accurate local field models of condensed systems. The effect of the local fields on the photoabsorption cross sections as the functions of the media density and structures has been studied in the present work. A substantial influence on the photoabsorption cross section has been found when the media density exceeds a critical density in the present unique model.

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Key words: algebraic method, local field effect, photoabsorption cross sections.

1 Introduction

The current understanding of photoabsorption processes has been established from theoretical research assuming the interaction of a laser pulse with gases at low pressures. For the isolated atom or molecule, the main characteristics of the photoabsorption process can be explained by the polarizability of the target. The photoabsorption cross section can usually be represented in terms of linear polarizability [1],

$$\sigma = \frac{4\pi\omega}{c} \zeta \quad (1)$$

where ζ is the imaginary part of the complex dynamic polarizability of an isolated atom or molecule, and is assumed scalar for simplicity. σ is the photoabsorption cross section, ω is the frequency of the laser pulse, and c is the light velocity. This is the fundamental expression for photoabsorption cross sections used for ideal gas in most of theoretical

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studies [2-6] and represents only the properties of isolated atoms or molecules in ideal gas.

However, that at sufficiently high intensities of the laser and high densities of the medium the polarizability of the target will be perturbed by the fields of other ions or atoms in the vicinity [7-10]. This impact of the surrounding medium on the photoabsorption spectrum is interesting in many respects [11-15]. A derivation of photoabsorption cross section for an atom embedded in a dielectric in which the atom and the nearby oscillators of the dielectric mutually interact via the electrodynamic field is needed. It is known from the Beer-Lambert's law that the number density of the medium significantly affects the measured cross-sections [16-21]. The photoabsorption cross section σ at photon energy ω is determined by the Beer-Lambert's law,

$$\sigma(\omega) = \frac{1}{Nl} \ln \left(\frac{I_0}{I} \right) \quad (2)$$

where I_0 is the intensity of the incident light, I is the attenuated intensity of the transmitted light, l is the transmitted length of light, and N is the number density of the system. Unless indicated atomic units are used throughout.

The experimental determination of accurate absolute values of photoabsorption cross sections is a difficult procedure using Beer-Lambert's law. One of the most troublesome problems encountered in atomic beam experiments is the accurate determination of the density of the atomic beam. In order to describe the response of a bulk material (high density), the effective permeability is needed. This can be found by averaging the effective dipole field over a large region. The results, known as the Clausius-Mossotti equation, or the Lorentz-Lorenz formula, can be used to relate the bulk effective permeability to the single atomic polarizability [16].

The functions chosen to relate the polarizability of the discrete dipoles to the dielectric properties of the bulk material have been developed in history [19-21]. The Clausius-Mossotti relation provides an exact function for the particular case of an infinite cubic lattice of dipoles in the dc limit, where the size of the dipoles divided by the radiation wavelength approaches zero [19]. Numerous schemes for modifying the Clausius-Mossotti relation have been proposed to improve the accuracy the coupled-dipole method for realistic, finite-sized scattering geometries [20]. Recently, Draine and Goodman developed an expression for polarizability of an infinite array of polarizable points so that the array exhibits the same dispersion relation as a continuum with dielectric constant ϵ . Draine and Flatau claimed in 1994 that this representation yields the best accuracy to date of these expressions for dipole polarizability [21].

A problem is that the electronic structure of these condensed system is not accurately known. Great effort are made to improve this description and the role of the spectroscopies. The data of the photoabsorption cross section is not enough, however, the available data will contain the influence effect model of the state of aggregation. Using the limited available data, in the present work, an algebraic method is developed to study the local field effect on the photoabsorption cross section in any media.

2 Algebraic models of the local field

In order to identify the influence of the state of aggregation on the observable properties of matter, Eq. (1) is not enough. That is, the photoabsorption cross sections σ of atoms in molecules or in solid should be expressed by the dielectric constant which related to the microscopic properties of atoms of these "macroscopic medium" based on Beer-Lambert's law [11]

$$\sigma(\omega) = \frac{\sqrt{2}\omega}{Nc} \sqrt{\sqrt{\epsilon'^2 + \epsilon''^2} - \epsilon'} \quad (3)$$

and another different formula for the photoabsorption cross section corrected for the presence of a medium using the Born-Oppenheimer approximation [12].

$$\sigma(\omega) = \left[\frac{n}{\epsilon} \left(\frac{E_e}{E} \right)^2 \right] \frac{8\pi^3\omega}{3c} I_{ba}(\omega) \quad (4)$$

where $I_{ba}(\omega)$ represents the square of the matrix element of emission transition from the initial quantum state a to the final state b , ω is the photon energy, N is the number density of the system, c is the speed of light, n and $\epsilon (= \epsilon' + i\epsilon'')$, are the index of refraction and the dielectric constant respectively. The factor $(E_e/E)^2$ describes the fact that the emitted electron is located in the medium of which the effective field E_e may differ from the average macroscopic electric field E . Because the Eq. (4) is dependent not only on the properties (n, ϵ) of the system but also on the external electric field E which is not the property of the system, it is not usually been used in theoretical calculations.

In order to deduce the general expression of the relative permittivity (dielectric constant) of a medium to its number density and mean dynamic polarizability, some models have been reviewed. For the special case, such as ideal gases, the dielectric constant without local field effects may be expressed as

$$\epsilon = 1 + 4\pi N\alpha. \quad (5)$$

For polarized atoms/molecules arranged in cubic crystals, the relation between polarizability and the dielectric function can be obtained using the well-known Clausius-Mossotti model which represents the interactions of the polarized particles in the crystals.

$$\epsilon = 1 + \frac{4\pi N\alpha}{1 - 4\pi N\alpha/3}. \quad (6)$$

This formula is found to work well for a wide class of dielectric liquids and gases. But it is the virtual cavity model, i.e., the local field, is modified by the presence of the cavity, but the modification of the field outside the cavity is disregarded. Hence the local field introduced in this way is not exactly the field that couples to the atom in reality.

On the contrary, the Glauber-Lewenstein model defines a more accurate relationship for dielectric constant and polarizability as

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{3\epsilon} = 4\pi N\alpha/3 \quad (7)$$

which is a real cavity model in which the modification of the fields outside and inside the cavity are taken into account in a consistent way. Recent experiments have been reported that the real cavity model may be favored.

Although the CM model is sufficient for quantities of ideal gas, it may still be crude for condensed system. Therefore we must look for a general model for complex dielectric constant. Since the classical CM model for cubic crystal only include induced dipole effect, if one adds induced multipole contributions and the overlapping effects of electron charge in the model, some small contributions in terms of power should be added. Therefore, Eq. (5) may be generalized exactly as

$$\epsilon_i = 1 + x \quad (8)$$

where $x = 4\pi N\alpha$. Eqs. (6) and (7) may also be expressed in series expansion respectively as

$$\epsilon_{cm} = 1 + x + \frac{1}{3}x^2 + \frac{1}{9}x^3 + \dots + \frac{1}{3^{n-1}}x^n + \dots \quad (9)$$

and

$$\epsilon_{gl} = 1 + x + \frac{1}{3}x^2 - \frac{1}{9}x^3 - \frac{1}{27}x^4 + \frac{5}{81}x^5 - \frac{1}{81}x^6 + \dots \quad (10)$$

Therefore, the dielectric constant ϵ may be generalized as

$$\epsilon = e_0 + e_1x + e_2x^2 + e_3x^3 + \dots + e_jx^j + \dots \quad (11)$$

where the coefficient $e_0 = 1$ and other coefficient e_j may have different value for these different models. The dielectric functions of condensed system of Eq. (11) can be simply expressed as

$$\epsilon(\omega) = \sum_{j=0}^{\infty} e_j x^j(\omega) \quad (12)$$

where the coefficients e_j are almost not vary for a wide frequency region for a given condensed system. For many condensed systems, a subset $[\epsilon(\omega)]$ and the dynamic polarizabilities $\alpha(\omega)$ of the m energies can be obtained through experimental measurement. Therefore, one can construct a equations by rewriting Eq. (12) in a matrix form

$$D = PE \quad (13)$$

where the solution matrix E and the dielectric functions matrix D are

$$D = \begin{pmatrix} \epsilon(\omega_1) \\ \epsilon(\omega_2) \\ \vdots \\ \epsilon(\omega_m) \\ \vdots \end{pmatrix}, \quad E = \begin{pmatrix} e_1 \\ e_2 \\ \vdots \\ e_j \\ \vdots \end{pmatrix} \quad (14)$$

and the matrix element of the $n \times 8$ coefficient matrix P is $P_{mj} = (4\pi N\alpha(\omega_m))^j$. Theoretically one may use all m known energies of the subset above to generate m coefficients by solving equations of Eq. (12) using standard algebraic methods without any approximation. However, the coefficient matrix E calculated in this way will be largely dependent on the selections of the subset, and the results will not be reliable.

The further questions at hand are: how does one obtain reliable e_j from such obtained accurate dielectric constants and polarizabilities of atoms? As one know that the property of the atom which buildups the condensed system usually varies with the energies of photon. However, For a given structure of the condensed system, the model which presents the interactions effects of atoms will vary with the photon energies very small, almost not vary with the photon energy. So, one can consider that the model of local field calculated for a given photon energies regions will apply properly to almost all the photon energies regions.

In this work, an alternative algebraic approach extended from [22] is proposed to evaluate the coefficients. Since the atomic/molecular dipole polarizability is complex valued, the real part ϵ' and the imaginary part ϵ'' of the dielectric function $\epsilon(\omega)$ may be expressed in general as

$$\epsilon' = \sum_{j=0}^{\infty} e'_j \left(4\pi N \sqrt{\eta^2 + \zeta^2} \right)^j \cos j\theta \quad (15)$$

$$\epsilon'' = \sum_{j=0}^{\infty} e''_j \left(4\pi N \sqrt{\eta^2 + \zeta^2} \right)^j \sin j\theta \quad (16)$$

where $\theta = \arctan\left(\frac{\zeta}{\eta}\right)$, e_j is the coefficient which maybe represent the collective influence effects of macroscopic matter. For Glauber-Lewenstein model and under the condition $|\epsilon| \geq 1$, the values of e_j are $e_0 = e_1 = 1$, $e_2 = \frac{1}{3}$, $e_3 = -\frac{1}{9}$, $e_4 = -\frac{1}{27}$, $e_5 = \frac{5}{81}$ and $e_6 = -\frac{1}{81}$, etc.

Because the initial e' will have different value for different set of particle polarizability

of ideal gas for given photon energy ω_p and density N of condensed system,

$$\begin{aligned}
 \epsilon'(\omega_1) &= \sum_{j=0}^{\infty} e'_j \left(4\pi N \sqrt{\eta^2(\omega_1) + \zeta^2(\omega_1)} \right)^j \cos j\theta \\
 \epsilon'(\omega_2) &= \sum_{j=0}^{\infty} e'_j \left(4\pi N \sqrt{\eta^2(\omega_2) + \zeta^2(\omega_2)} \right)^j \cos j\theta \\
 &\vdots = \vdots \\
 \epsilon'(\omega_m) &= \sum_{j=0}^{\infty} e'_j \left(4\pi N \sqrt{\eta^2(\omega_m) + \zeta^2(\omega_m)} \right)^j \cos j\theta \\
 &\vdots = \vdots
 \end{aligned} \tag{17}$$

They can be rewritten in matrix form

$$\Delta = AE' \tag{18}$$

where the Δ matrix and the solution (unknown) E matrix respectively are

$$\Delta = \begin{pmatrix} \epsilon'(\omega_1) \\ \epsilon'(\omega_2) \\ \vdots \\ \epsilon'(\omega_m) \\ \vdots \end{pmatrix}, \quad E' = \begin{pmatrix} e'_1 \\ e'_2 \\ \vdots \\ e'_j \\ \vdots \end{pmatrix} \tag{19}$$

The elements of the coefficient matrix A are

$$A_{mj} = \left(4\pi N \sqrt{\eta^2(\omega_m) + \zeta^2(\omega_m)} \right)^j \cos j\theta \tag{20}$$

The solution vector E can then be obtained by solving Eq. (18) iteratively using standard algebraic method.

On the other hand, the initial ϵ'' also has the same matrix form as above,

$$\Pi = BE'' \tag{21}$$

where the Π matrix and the solution (unknown) E matrix respectively are

$$\Pi = \begin{pmatrix} \epsilon''(\omega_1) \\ \epsilon''(\omega_2) \\ \vdots \\ \epsilon''(\omega_m) \\ \vdots \end{pmatrix}, \quad E'' = \begin{pmatrix} e''_1 \\ e''_2 \\ \vdots \\ e''_j \\ \vdots \end{pmatrix} \tag{22}$$

The elements of the coefficient matrix B are

$$B_{mj} = \left(4\pi N \sqrt{\eta^2(\omega_m) + \zeta^2(\omega_m)} \right)^j \sin j\theta. \quad (23)$$

Then, the other solution vector E can also be obtained by solving Eq. (21) iteratively using standard algebraic methods.

In order to reduce the reliability on the selections of the subset, There are two method to be used in this work. On one hand, According to Eq. (12), the calculated coefficients e'_j and e''_j must be equal. So the best solution vector E our of the N sets of solutions should best satisfy the followings requirements.

$$E' = E'' \quad (24)$$

where the E' and E'' are calculated by Eq. (18) and Eq. (21) using the same subset separately. On the other hand, for all the coefficients calculated from all sets of data, one must average these coefficients and uses the average to represent the real coefficient.

Since accurate experimental dielectric constant expressed as the series expansion of atomic polarizability to unlimited order include most important physics such as the atom-atom interaction, the dipole-dipole interaction, and since these carry all local field information, the expression obtained using the AM should best reproduce the subset and correctly generate other dielectric functions of other energies, which may be difficult to obtain experimentally.

3 Algorithm and Implementation

Our experience show that it is reasonable enough to use the first eight powers of Eq. (12) for $j = 0, 1, 2, \dots, 7$. This means that one should choose 8 of the m known energies at a time should be known to solve Eq. (12). There are C_m^8 groups of energies that can be chosen. Usually it is enough to select N (far less than C_m^8) groups of energies out of the m energies of the subset to find the best set of the dielectric. On the other hand, the matrix P may both small and very large matrix elements for $j > 7$ such that the algebraic calculations of these elements performed using computers with 32-digit precision may introduce notable numerical errors in dielectric constants. Matrix calculations involving such matrix elements would produce non-negligible errors. For these reasons, we choose the series expansions of 8 [22-24].

If there are n ($n \geq 3$) sets of polarizabilities and dielectric constants, In order to obtain the physically accepted local field models, an alternative algebraic method is suggested as follows [22-24]:

(a) Choose 3 of the n known energies at a time to solve Eq. (18) and Eq. (21) separately. Usually it is enough in this step to select some groups of energies out of the n energies of the subset to find the best set of dielectric constant which consistent with the Eq. (24). Then one can obtain some sets of the coefficients, e_0, e_1, e_2 .

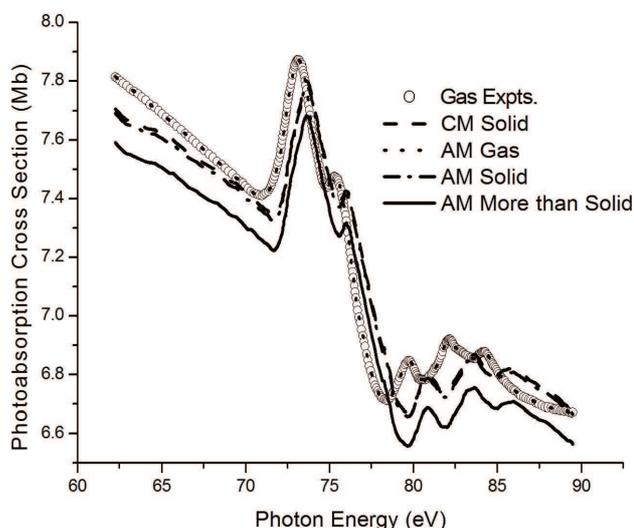


Figure 1: Comparison of the total photoabsorption cross sections for copper under several models.

(b) Choose 4 of the n known energies at a time solve Eq. (18) and Eq. (21) separately. In this step, perhaps one can obtain the coefficient e_0, e_1, e_2, e_3 which consistent with the Eq. (24).

(c) As the same way, choose m of the n known energies at once time, one can get the coefficients $e_0, e_1, e_2, e_3, \dots, e_m$. Once the requirements in Eq. (24) are not satisfied, the final results are $e_0, e_1, e_2, e_3, \dots, e_{m-1}$. and the equation

$$\epsilon(\omega) = e_0 + e_1x + e_2x^2 + e_3x^3 + \dots + e_mx^m \quad (25)$$

is the final algebraic model of the local field of the given condensed system.

Once the requirements in Eq. (24) are satisfied, the AM approach generates physically well-behaved local field models. As an example, Fig. 1 shows the comparison of the copper photoabsorption cross sections among the ideal gas experimental results. The CM model solid calculations and the present AM results under three conditions. These theoretical results are calculated from the same atomic polarizabilities which are calculated from the ideal gas experimental data using Eq. (1). The dielectric constants used in AM model are calculated from the ideal gas data. Under the same conditions, the present AM method reproduces almost the same results with the ideal gas and solid CM one respectively. All of these theoretical photoabsorption cross sections will be convergent to the gas experimental results.

In the ideal gas number density, the theoretical photoabsorption cross section of AM model are not considerably different from those obtained from the ideal gas experiments. When the number density increases larger than that of solid state in the AM model, the

AM result show the same variation with the number density as the CM model. This indicates that the present AM model not only can reproduce the CM model, but can represent the same local field effect in the media. Compared with the results obtained in the CM model and the AM model, the present algebraic method shows more correct behaviour that is dependent on actual experimental condition.

4 Discussion and Summary

This study proposes an alternative algebraic method to study accurate local field model based on an accurate limited experimental/theoretical input data set. The AM generates accurate local field effect using a standard algebraic approach without any mathematical and or physical approximations. The accuracy of the AM constants and local field factor is uniquely dependent on the quality of the input experimental/theoretical data. One may always select N groups of energies out of the m known energies of a subset of the full energy dielectric functions for a condensed system and solve linear equations to obtain N sets of coefficients.

In the present work, the behaviour of the variation of the photoabsorption cross section of atomic copper with number density has been reproduced. The present study not only gives a new algebraic method to study the condensed photoabsorption process of atoms in special condition, but also can obtain the accurate models of the local field in the condensed.

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