

Density dependence of the dielectric constant of rare-gas crystals

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A local-density approximation scheme is proposed to compute, from first principles, the in-crystal polarizabilities of rare-gas atoms. The scheme is applicable to condensed, closed-shell systems in general, ordered or disordered. The method is illustrated by computing the density dependence of the dielectric constant of crystalline Ar. Excellent agreement with experimental results is found.

I. INTRODUCTION

Linear-response calculations based on the local-density approximation (LDA) have had an impressive series of successes. First-principles computations of the dielectric properties of atoms,¹⁻³ ions,⁴ semiconductors,⁵ and small metal particles⁶ have yielded results in good agreement with experimental values.

For ionic crystals the in-crystal polarizabilities have been evaluated^{4,7,8} by adding the spherically averaged Madelung and overlap potentials to the atomic potential. Mahan^{4,7} introduced the overlap contribution through suitable pseudopotentials for the neighboring ions. Fowler and Madden⁸ did so by considering the central ion and the nearest neighbors as a cluster embedded in a lattice of point ions. In a strict sense, neither procedure is strictly self-consistent in that the central ion and the rest of the ions are not treated on an equal footing. An alternative and more elaborate crystalline treatment would be a frozen-electric-field calculation along the lines of the work by Kunc and Resta.⁹

In Sec. II of this paper we present a self-consistent scheme for the computation of the ground-state properties of closed-shell atoms and ions in the condensed state. The method is readily applicable to ordered as well as disordered phases. In Sec. III the method is applied to evaluate the density dependence of the dielectric constant of crystalline Ar. Comparison with experimental results is made. The last section contains a summary of our main results.

II. SELF-CONSISTENT SCHEME

As mentioned in the Introduction, our interest is in developing a fully self-consistent, simple scheme within the LDA to evaluate the ground-state properties of closed-shell condensed media. In particular, we wish to address the first-principles computation of linear and nonlinear dielectric susceptibilities of closed-shell atoms and ions in different environments. The importance of these quantities for the evaluation of Raman scattering intensities has been emphasized recently.^{10,11}

The requirement of simplicity is attained by retaining the localized picture of the electronic levels. Thus, dispersion of the occupied orbitals is completely neglected. For

the optical properties of interest to us this is not a serious limitation. Our scheme is in a certain sense a "mean-field" theory in that we demand that all like ions be identical when self-consistency is reached. For specificity we will confine our attention to a neutral assembly of rare-gas atoms in what follows.

The scheme is loosely based on the Kohn-Sham density-functional formulation.¹² The electronic energy of the condensed system of closed-shell ions is written as a functional of the total electronic density $n(\mathbf{r})$,

$$E = T_s[n] + U_{\text{ext}} + U_H + U_{\text{xc}}[n], \quad (2.1)$$

$$U_{\text{ext}} = \int n(\mathbf{r})V_{\text{ext}}(\mathbf{r})d^3r, \quad (2.2)$$

$$U_H = \frac{e^2}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \quad (2.3)$$

In light of the closed-shell, localized electronic configurations of interest we split up the density into that of the "central" ion and that of the others:

$$n(\mathbf{r}) = n_0(\mathbf{r}) + \sum_{i(\neq 0)} n_i(\mathbf{r}). \quad (2.4)$$

Further, we rewrite the kinetic energy as

$$\begin{aligned} T_s[n] &= T_s[n_0] + \{T_s[n] - T_s[n_0]\} \\ &\equiv T_s[n_0] + U_K[n, n_0], \end{aligned} \quad (2.5)$$

where now, U_K contains the kinetic-energy contribution arising from the presence of the surrounding atoms. We then perform a partial minimization of E with respect n_0 , while keeping all other n_i fixed. By introducing the Kohn-Sham orbitals $\phi_{\alpha,0}$ for the central density.

$$n_0(\mathbf{r}) = \sum_{\alpha(\text{occ})} |\phi_{\alpha,0}(\mathbf{r})|^2, \quad (2.6)$$

in terms of which

$$T_s[n_0] = \frac{-\hbar^2}{2m} \sum_{\alpha} \int \phi_{\alpha}^*(\mathbf{r}) \nabla^2 \phi_{\alpha}(\mathbf{r}) d^3r, \quad (2.7)$$

we are then led to the Kohn-Sham equations

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + V_{\text{eff}} \right] \phi_{\alpha,0}(\mathbf{r}) = \epsilon_{\alpha} \phi_{\alpha,0}(\mathbf{r}). \quad (2.8)$$

In the above

$$V_{\text{eff}} = V_{\text{ext}} + V_H + V_{\text{xc}} + V_K. \quad (2.9)$$

Here V_K is a "kinetic potential" due to the surrounding atoms:

$$V_K = \delta U_K[n, n_0] / \delta n_0, \quad (2.10)$$

where $U_K[n, n_0]$ is defined in Eq. (2.5). Note that this is the only repulsive contribution to V_{eff} arising from the presence of the neighbors. In light of the localized nature of the orbitals the isolated atom boundary conditions can be safely employed for the ϕ_α . The requirement that all atoms in the assembly are to be identical is imposed through the condition

$$n_i(\mathbf{r}) = n_0(\mathbf{r} - \mathbf{R}_i), \quad (2.11)$$

where \mathbf{R}_i is the position of the i th atom. Equations (2.6), (2.8), and (2.11) then represent a set of equations that have to be solved self-consistently.

Note that the above scheme defines a procedure for minimizing the free energy for a fixed configuration of the nuclei. The method of simulated annealing recently proposed by Car and Parrinello¹³ for the simultaneous minimization of the free energy with respect to the electronic and nuclear degrees of freedom can readily be applied here if desired. Work along these lines is in progress.

Turning now to the practical aspects, many of the approximations commonly made are used here as well. Firstly, a local-density approximation for the exchange-correlation potential is made,

$$V_{\text{xc}}(\mathbf{r}) = V_{\text{xc}}^{(h)}(n(\mathbf{r})), \quad (2.12)$$

where the right-hand side corresponds to the exchange-correlation potential for the homogeneous electron gas at the appropriate local density. In the same spirit, we make a local-density approximation for V_K , the kinetic contribution of the neighbors:

$$V_K[n, n_0] = \frac{\hbar^2}{2m} (3\pi^2)^{2/3} \{ [n(\mathbf{r})]^{2/3} - [n_0(\mathbf{r})]^{2/3} \}, \quad (2.13)$$

where the result for the kinetic energy of the homogeneous electron gas has been used.¹⁴ Thus, our method is similar in spirit to that of Gordon and Kim.¹⁵ The primary, and important difference is that we treat the kinetic energy of the central electrons exactly in the Kohn-Sham scheme.

The next approximation made for practical reasons is that of spherical averaging. Since the isolated atomic potential and density are spherically symmetrical, we replace $n(\mathbf{r})$ and $V_H(\mathbf{r})$ by their spherical averages in Eq. (2.8). These can be augmented with higher spherical harmonic components if necessary. With the spherical approximation the problem is no more difficult than that for the isolated atom. The practical procedure then begins with $n_0(r)$ and $V_{H,0}(r)$ computed in the LDA for an isolated atom. From these the spherical average

$$n(r) = n_0(r) + \frac{\rho}{2r} \int d^3R \frac{g(R)}{R} \int_{|R-r|}^{R+r} r' n_0(r') dr', \quad (2.14)$$

is evaluated. Here ρ is the average density of atoms in the system, and $g(R)$ is the radial distribution function. In arriving at Eq. (2.14) the familiar Löwdin α expansion has been utilized.¹⁶ Similarly, the spherically averaged Hartree contribution is evaluated by replacing $n_0(r)$ in Eq. (2.14) by $V_{H,0}(r)$. These are used to compute $V_{\text{eff}}(r)$ in Eq. (2.8), from which new Kohn-Sham orbitals, and a new density for the central atom are obtained. This new density is used in Eq. (2.14) and so on until self-consistency is attained.

One drawback of the above scheme, which comes about because of the local-density approximation, is the neglect of long-range, dispersive (van der Waals) forces between the atoms. The problem is that in the local-density approximation the correlation is taken into account only in the overlap region. As has been discussed in the context of the Gordon-Kim electron gas theory of intermolecular forces,¹⁵ the local-density approximation appears to be adequate for distances up to about the minimum of the interatomic potential.¹⁷ For interatomic potential energy the long-range correlations lead to the familiar R^{-6} van der Waals contribution at large distances. Similarly, for the mutual polarizability of a pair of neutral atoms there is a R^{-6} correlation contribution at large distances.¹⁸ Inclusion of these smaller effects at the self-consistent level is rather cumbersome. The error involved, in any case, may be estimated *a posteriori* to ascertain its smallness, or approximate schemes to include them can be devised. Note that for ionic systems (e.g., alkali halides) the dispersive forces are indeed rather insignificant.

Once the modified atomic potential and density are obtained in the above manner, the polarizability in the condensed phase may be obtained either by the Greens's function^{1,2} or the modified Sternheimer method.³ In either case, one calculates the first-order density change $n_0^{(1)}(\mathbf{r})$ of the electronic cloud of the atom caused by a local electrical field. There is an associated change in the self-consistent effective potential to the same order,³ $V^{(1)}$.

A full application of our "mean-field" scheme involves the presence in $V^{(1)}$ of a term arising from the distortion of the surrounding atoms due to the electric field. This results in an overlap contribution to the dipole-induced-dipole (DID) part of the in-crystal polarizability.¹⁸ In fact, the Clausius-Mossotti relation,

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi\rho\alpha}{3}, \quad (2.15)$$

which is used to relate α to the measured dielectric constant ϵ , only embodies a point-dipole contribution to the DID polarizability. In the illustrative numerical results presented in the next section the distortion contribution of the neighbors to the DID polarizability of the central atom has been neglected. We expect it to be of minor importance in comparison with the compression of the central atom caused by the undistorted neighboring atoms. The dependence of ϵ on thermodynamic parameters may

be evaluated in the above scheme through its dependence on ρ and $g(R)$. The method will be illustrated in the next section through the evaluation of the density dependence of ϵ for solid Ar.

III. DENSITY DEPENDENCE OF ϵ IN SOLID ARGON

To test the procedure outlined in the preceding section we have computed the density dependence of the static dielectric constant of crystalline Ar. Detailed measurements of $\epsilon(\omega)$ for a range of densities were carried out many years ago.¹⁹ The only previous theoretical work on the subject is by Keil,²⁰ who used a non-self-consistent tight-binding approach. Not surprisingly, the absolute value of the calculated polarizability was in poor agreement with experiment. The experimental data are conveniently presented through the so-called Lorentz-Lorenz function,¹⁹

$$F_{LL} = \frac{1}{\rho} \frac{\epsilon - 1}{\epsilon + 2} \equiv \frac{4\pi N_A \alpha}{3}, \quad (3.1)$$

where ρ is the density in mol/cm³, and N_A is Avogadro's number. Thus, any residual dependence of F_{LL} on density arises from the density dependence of α itself through overlap effects. We, therefore, compute α for an Ar atom in the crystal as a function of lattice constant. The lattice constant enters the theory through $g(R)$ in Eq. (2.14). Specializing to an ordered crystal, Eq. (2.14) may be written as

$$n(r) = n_0(r) + \sum_i \frac{N_i}{2R_i r} \int_{|R_i - r|}^{R_i + r} r' n_0(r') dr', \quad (3.2)$$

where N_i is the number of neighbors in the i th shell at a distance of R_i .

The LDA procedure for computing α via the modified Sternheimer method³ has been discussed at length in the literature and will not be repeated here. We used the Perdew-Zunger parametrization²¹ of the Ceperly-Alder²² results of the homogeneous electron-gas exchange-correlation potential. For the ground-state calculation we also used the self-interaction correction (SIC) as proposed by Perdew and Zunger.²¹ The merits of using SIC at various levels in the calculation of polarizabilities have been assessed recently by us.²³ We imposed a self-consistency requirement of convergence of the total energy to one part in 10^6 .

As mentioned in the preceding section the method can be expected to give a reasonable estimate of cohesive energy even with the neglect of long-range correlation effects. This should be especially true of the less polarizable atoms since the dispersive contribution depends on α^2 . Indeed, for Ne we calculate the binding energy to be 0.0013 Ry/atom, compared to the experimental value of 0.0015 Ry/atom. For Ar, on the other hand, the calculated value is 0.0040 Ry/atom, compared to 0.0059 Ry/atom. A suitable method for including the long-range part is presently under investigation.

Turning now to the results of the polarizability calculations for Ar, we show the computed values of F_{LL} [see

TABLE I. Density dependence of the Lorentz-Lorenz function for solid Ar.

ρ (10^{-2} mole/cm ³)	F_{LL}^{calc} (cm ³ /mole)	$F_{LL}^{\text{expt}^a}$ (cm ³ /mole)	$\frac{F_{LL}^{\text{calc}}}{F_{LL}^{\text{expt}}}$
~ 0	4.365	4.217	1.035
4.093	4.321	4.156	1.040
4.170	4.311	4.148	1.039
4.235	4.307	4.144	1.039
4.293	4.303	4.138	1.040
4.343	4.299	4.132	1.040
4.385	4.294	4.124	1.041
4.416	4.289	4.117	1.042

^aAll except the first value are from Ref. 24. First value is from Ref. 25.

Eq. (3.1)] for various densities in the second column of Table I. The third column contains the experimental results (for $\lambda = 5461$ Å) of Sinnock and Smith.²⁴ The free-atom value is from Leonard²⁵ (for $\lambda = 5463$ Å). The last column gives the ratio of the calculated and experimental values. Note that for all densities the relative errors are within 4%, and consistent with the error in computing the free-atom value itself. Since we are interested in the relative variation, we have not extrapolated the experimental values to their zero-frequency values for comparison with theory. In any case, the dispersion is less than a few percent. Note that the in-crystal value of α is reduced by $\sim 2\%$ (at the highest density, or lowest temperature) relative to that of the free atom. This is the result of "overlap compression."

IV. SUMMARY

We have presented a simple, local-density scheme for the first-principles computation of the properties of condensed matter consisting of closed-shell atoms or ions. The method can be applied to calculate, e.g., the dielectric properties of solid or liquid (molten) rare gases and alkali halides. The thermodynamic information enters the microscopic electronic calculation through the pair distribution function. The scheme is an effective medium approach in that all like atoms in the medium are considered to be identical, unlike in a cluster calculation. Computationally, the procedure is no more difficult than that for isolated atoms. We have used the method to evaluate the density dependence of the polarizability of solid Ar as an illustration. Good agreement with experimental data is found.

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