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Ground- and excited-state properties of solid argon under pressure

R. LeSar
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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A self-consistent perturbation model for calculating the ground- and excited-state electronic properties of molecular and rare-gas crystals is presented. A tight-binding approximation is used, in which the effects of the crystal potential, calculated with local-density functionals, are included as a perturbation on the molecules (or atoms). The molecular (atomic) wave functions are then computed from standard Hartree-Fock theory. For the case of solid argon under pressure, a decrease in atomic volume causes a gain in free energy, which is partially balanced by the energy required to compress the atom. Calculated exciton energies for Ar disagree by only 2.5% with experimental values at zero pressure.

I. INTRODUCTION

In the last two decades much progress has been made in the theory of gas-phase chemical kinetics. Many models[1] have been developed to explain and predict the outcome of reactive collisions between simple molecules. However, because of the fundamental differences between the chemistry of isolated molecules and molecules on a crystal lattice, gas-phase concepts are not directly applicable to reactions in solids, especially the high-pressure solids found in the interiors of planets, in detonation shock waves, or in diamond anvil cells. Recent experimental results[2] on CO and SO_2 at high pressures show that photochemical reactions occur in these materials only after the crystals undergo a structural phase transition. A recent theoretical calculation[3] suggests that the H_6 molecule, which cannot exist for more than one vibrational period in the gas phase, might be stabilized in a high-pressure solid. These results show that the reaction potential surfaces are much different in the solid than in the gas phase, with certain reaction pathways potentially blocked by the other molecules in the solid. Thus, a comprehensive theory of the chemical reactivity of such systems must treat both the electronic structure of the constituent molecules and the crystal structure.

Crystal structures of molecular solids can be accurately calculated by a recently reported *ab initio* theory.[4] This method, which is based on the Gordon-Kim[5] model for calculating intermolecular forces, gives very good results for the structure and energy of molecular crystals, without the prior determination of pair interaction potentials. Since the only input is the electronic density of the constituent molecules, perturbations of the molecules are easily incorporated in the crystal-structure calculation.

Significant progress has been made recently in calculating the electronic structure of solids. For metals, various techniques [Korringa-Kohn-Kostoker (KKR), augmented-plane-wave (APW), and linear muffin-tin orbital techniques (LMTO)] have been developed for finding the electronic bands, cohesive energies, pressure-volume relations, and other properties with deviations of a few percent.[6] Pseudopotential calculations have been employed to calculate the properties of semiconductors, such as Si (Ref. 7) and Ge (Ref. 8) with errors of 1% or so, and have been used to give reasonably accurate predictions of phase transitions. However, none of these methods are entirely suitable for calculating the electronic structure of molecular crystals. Band-structure calculations for metals, as usually applied,[9] employ a muffin-tin approximation, assuming spherical symmetry about each lattice point. Because of the nonspherical shapes of molecules, a spherical approximation is not a particularly good starting point for the calculation of their properties. Pseudopotential calculations can be used, but require large basis sets, and are therefore computationally costly.[7] The same criticism applies to the Hartree-Fock self-consistent-field methods that have been proposed.[10] These latter calculations are numerically difficult, and the approximations necessary to overcome this problem make the theories either inaccurate or impractical for most crystals. Also, most electronic structure methods[11] cannot, in their present formulations, be easily used to study the excited states (excitons) of the molecules in the crystal.

One of the difficulties in dealing with the electronic structure of molecular crystals is to take into account the molecular character as well as the long-range forces in the crystal. One can approach the problem by focusing on the solid and using as a basis the solution to the crystal Hamiltonian, or one can focus on the molecules and treat the crystal as a perturbation. Here we take the latter approach. Local-density functionals are used to calculate the crystal potential, which in turn is used as a perturbation in calculating the molecular wave function by standard Hartree-Fock theory. The ground-state crystal structure of the system is found self-consistently by including changes in structure due to changes in the constituent molecules. Excited-state transitions are calculated for the molecule in the crystal field of the ground-state molecules.

Here we develop the method and apply it to a rare-gas crystal (Ar) as a function of pressure. Although Ar can be treated by standard band-structure techniques, the distortions of the atomic wave functions make it a prototype for our molecular technique. The calculations are compared to experimental structural data and to low-pressure exciton data. In Sec. II, the crystal structure model is outlined, while in Sec. III the crystal-perturbation (CP) model is described. Results on ground- and excited-state properties are given in Sec. IV, and are discussed in Sec. V. All quantities, unless noted, are given in a.u. with 1 bohr=0.529 177 Å and 1 hartree=2 Ry=27.2116 eV.

II. CRYSTAL-STRUCTURE CALCULATIONS

Crystal structures as a function of pressure were calculated with a recently reported theory, based on the Gordon-Kim (GK) electron-gas model,[5] that gives excellent agreement with experiment (1–3 % discrepancy in both lattice energy and structure) for a large number of molecular[4] and ionic[12] crystals. It is assumed in the GK model that the total electronic density of a crystal can be approximated by the sum of the electronic densities of the constituent molecules as

$$\rho_T(\vec{r})=\sum_i\sum_{\vec{l}}\rho_i(\vec{r}-\vec{r}_{il}) , \qquad (1)$$

where $\rho_T(\vec{r})$ is the total electronic density at point $\vec{r}$, the sum over i is a sum over all the molecules in the unit cell, $\vec{l}$ is a lattice vector, and ρ_i is the electronic density of the ith molecule in the unit cell. The crystal electron-gas energy can be written as

$$W_j=\int_V d\vec{r}\left[\rho_T(\vec{r})E_j[\rho_T(\vec{r})]-\sum_i\sum_{\vec{l}}\rho_i(\vec{r}-\vec{r}_{il})E_j[\rho_i(\vec{r}-\vec{r}_{il})]\right] ,$$

where E_j is the appropriate energy density functional (kinetic, exchange, or correlation) for a uniform electron gas and V is the unit-cell volume. The forms of these functionals will be given in Eq. (5) below. The electrostatic energy is divided into a point-Coulomb (Madelung) term and a non-point-Coulomb term. The total interaction energy per unit cell is calculated directly, obviating calculation of the pair potentials. The only input is the electronic density of each constituent molecule.

For crystals involving neutral molecules (or atoms), the long-range dispersion (van der Waals) energy must be included. We approximate these interactions by summing over the pair potentials $V=-C_6/r^6$, where C_6 is the dispersion coefficient and r the distance between the pairs. We do not include the electron-gas correlational energy since it is included in the disperion-energy term. This approximation may break down at very small separations where the long-range r^{-6} form of the dispersion energy is no longer valid.[4(b)] We neglect many-body contributions to the dispersion energy.

At low pressures, the properties of crystals made up of neutral molecules or atoms can be accurately calculated using gas-phase electronic densities for the molecules (atoms) in the crystals and gas-phase dispersion coefficients. At high pressures there are larger perturbations of the molecules in the crystal, and the crystal-molecular electronic densities must be used in the electron-gas calculation of the crystal structure. Changes in the dispersion coefficient can be approximated from relations given by the Drude[13] for dispersion energies and the Kirkwood formula[14] for the atomic and molecular polarizabilities. For atoms, the polarizability is given by

$$\alpha=\frac{4}{9N}\langle r^2\rangle^2 ,$$

where N is the total number of electrons and $\langle r^2\rangle$ is the average of r^2 over the atomic electronic distributions. We scale this result to the experimental polarizability and find for α as a function of pressure

$$\alpha(P)=\alpha_g\left[\frac{\langle r^2\rangle_p}{\langle r^2\rangle_g}\right]^2 . \qquad (2)$$

Here, α_g is the gas-phase value of the polarizability and $\langle r^2\rangle_g$ the average over the gas-phase electronic distributions. We find $\langle r^2\rangle_g$ from Hartree-Fock calculations on the isolated atom. The average of r^2 over the crystal atomic wave functions $\langle r^2\rangle_p$ changes as a function of pressure. The dispersion coefficient is given, in the Drude model,[13] by

$$C_6=\frac{3}{4}\frac{Q_a}{\sqrt{m}}\alpha^{3/2} ,$$

where Q_a is the number of electrons in the valence shell of the atom and m is the effective mass of the valence shell found by fitting experimental data. If we assume that Q_a and m are constants, independent of changes in the electronic distributions, we find

$$C_6(P)=C_{6,g}\left[\frac{\langle r^2\rangle_p}{\langle r^2\rangle_g}\right]^3 , \qquad (3)$$

where $C_{6,g}$ is the gas-phase dispersion coefficient. Below, we shall use this relation to calculate pressure-dependent changes in the dispersion constant for use in computing the crystal structure.

We note that this method of calculating crystal structures is consistent with the tight-binding approximations made in this paper. It is assumed that the atoms or molecules in the crystal dominate the crystal properties. We calculate the interaction of these molecules, rather than the total crystal energy, which obviates the solution of the many-electron crystal Hamiltonian, and thus makes possible calculations on complicated systems.

III. CRYSTAL-PERTURBATION MODEL

A. General

We assume that the electrons in the molecular crystal are tightly bound to their molecular sites. This assumption limits the model to regimes where the band gap is still large. We then determine the way the crystal environment perturbs a molecule by performing a Hartree-Fock self-consistent-field (SCF) calculation on the molecule in a crystal field. The crystal potential is calculated with local-density functionals, and is included in the SCF calculation only in the one-electron integrals, thereby lengthening, only slightly, the time needed for the molecular or atomic calculation.

As in the GK model, Thomas-Fermi-Dirac (TFD) functionals[15] are used and the total crystal energy can be written as

$$E=\int \{\rho_\tau(\vec{r})(E_k[\rho_\tau]+E_x[\rho_\tau]+E_c[\rho_\tau])+\rho_{\tau'}\Phi(\rho_{\tau'})\}d\vec{r}\ , \tag{4}$$

where the density functionals are, for the kinetic, exchange, and correlational functionals, respectively,[5]

$$E_k=\tfrac{3}{10}(3\pi^2)^{2/3}\rho^{2/3}=C_k\rho^{2/3},\quad E_x=-\frac{3}{4}\left[\frac{3}{\pi}\right]^{1/3}\rho^{1/3}=-C_x\rho^{1/3}\ ,$$

$$E_c=\begin{cases}0.0311\ln r_s-0.048+0.009r_s\ln r_s-0.01r_s, & 0\le r_s\le 0.7\\ -0.061\,56+0.018\,98\ln r_s, & 0.7\le r_s\le 10\\ -0.438r_s^{-1}+1.325r_s^{-3/2}-1.47r_s^{-2}-0.4r_s^{-5/2}, & 10\le r_s\end{cases} \tag{5}$$

where $r_s=(\frac{3}{4}\pi\rho)^{1/3}$. The total electronic density ρ_τ is given in Eq. (1) and the total charge density $\rho_{\tau'}$ is given by

$$\rho_{\tau'}(\vec{r})=\sum_i\sum_{\vec{l}}Z_i\delta(\vec{r}-\vec{r}_{il})-\rho_\tau(\vec{r})\ ,$$

where Z_i is the nuclear charge of the ith atom and $\delta(\vec{r})$ is the Dirac δ function. The total electrostatic potential is Φ_τ. The different terms (kinetic, exchange, and correlation) are scaled to give agreement with atomic SCF energies.[16] The scaling factors for interacting pairs of atoms are found by comparing the density-functional energies, found by integration of the energy density functional in Eq. (5), with the appropriate SCF energies for the atom isoelectronic with the pair. This scaling is an approximate correction for the inadequacies of the density functionals in determining the pair interaction potential with the GK model.[16] These factors are used in calculating the crystal structure, and, for consistency, in finding the crystal potential.

The TFD crystal potential H_c can be found by taking the functional derivative of Eq. (4) with respect to ρ_τ,

$$H_c=\tfrac{5}{3}C_k\rho_\tau^{2/3}-\tfrac{4}{3}C_x\rho_\tau^{1/3}+E_c'(\rho_\tau)+\Phi_\tau\ , \tag{6}$$

where E_c' is the derivative of $\rho_\tau E_c(\rho_\tau)$. The crystal interaction potential is found by subtracting the TFD potential of the atom or molecule at the origin. This molecular (atomic) potential H_m has the same form as Eq. (6) but with $\rho_m(\vec{r})$, the molecular (atomic) electronic density, replacing ρ_τ. The crystal interaction potential is

$$V(\vec{r})=H_c-H_m\ . \tag{7}$$

This perturbation is added to the molecular (atomic) Hartree-Fock Hamiltonian and the crystal-molecular (atomic) wave function determined using standard free-molecular Hartree-Fock techniques.

B. Application to argon

We now illustrate the method for the rare-gas crystal Ar. For computational ease we represent $V(\vec{r})$ as an expansion in a set of orthogonal polynomials. For Ar in the fcc lattice, it is most convenient to use the Kubic harmonics, which are linear combinations of the spherical harmonics.[17] We then have

$$V(\vec{r})=\sum_n K_n(\theta,\phi)V_n(r)\ , \tag{8a}$$

and

$$V_n(r)=\int_0^{2\pi}\int_0^{\pi}V(\vec{r})K_n(\theta,\phi)\sin\theta\, d\theta\, d\phi\ . \tag{8b}$$

For a fcc lattice only even terms in the expansion are nonzero, and the $n=2$ term vanishes. The first two Kubic harmonics are the following:[18]

$$K_0=Y_{00},\quad K_4=(\tfrac{7}{12})^{1/2}[Y_{40}+(\tfrac{5}{14})^{1/2}(Y_{44}+Y_{4\bar{4}})]\ .$$

Here the Y_{lm} are the spherical harmonics. In the SCF calculation of the atom in the crystal field, the crystal potential is included in one-electron integrals over products of the atomic orbitals. The integrals over terms with $n\ge 4$ are zero for Ar, unless excitations to d orbitals are included. Here we consider the ground and first few excited states of Ar, so we keep only the spherically symmetric $V_0(r)K_0$ term. The crystal potential is determined by summing the electronic density and potential in the crystal and then finding the density-functional and electrostatic terms. The expansion coefficients $V_0(r)$ are determined by numerical integration using a two-dimensional Gauss-Legendre (GL) quadrature[19] at a set of radial distances corresponding to the one-dimensional GL quadrature used to calculate the SCF perturbation integrals.

All integrals were calculated to about 1% accuracy. We used a standard SCF program with the orbitals expanded in Slater functions.[20] The energies of the excited states were found from the Slater coefficients for open-shell interactions.[21] The wave function for Ar, proposed by Clementi and Roetti[22] with two added 4s functions, was used for all calculations. This wave function gives the Hartree-Fock limit for the isolated atom. We optimized the outer-orbital exponents for all calculations. For the ground-state calculations, contributions from the first three neighbor shells were included. At 500 kbar, inclusion of the second two shells changed the energy by only 6×10^{-5} hartrees out of a total energy of about -526.719 hartrees. For the excited states, however, more shells were necessary to obtain convergence, as discussed below.

The calculational procedure is straightforward. The pressure-volume curve is determined using gas-phase Ar electronic densities and the gas-phase dispersion coefficient ($C_6 = 64.8$).[23] Many-body dispersion terms were neglected, although Aziz[24] has estimated them to make a 2% contribution to the total dispersion energy in the zero-pressure solid. These calculations are done by minimizing the free energy ($G = E_l + PV$) at a given pressure, where the lattice energy E_l is a sum of the electron-gas terms, the Coulomb terms, and the dispersion energy. At lattice parameters corresponding to a given pressure, the crystal potential is calculated, followed by a SCF calculation which gives the crystal atomic wave function for that pressure. A new crystal volume is then computed for that pressure using this new atomic wave function and the new crystal dispersion constant found from Eq. (3). A new potential is generated and the procedure is iterated until we have a minimum crystal-free energy, where the change in atomic self-energy due to changes in the wave function must be included in the crystal energy. The change in self-energy E_s is given by

$$E_s = E_{\rm cr}(P) - E_{\rm scf}({\rm gas}) \,, \qquad (9)$$

where $E_{\rm cr}$ is the SCF electronic energy of the crystal wave function (not including the interaction energy with the crystal potential) and $E_{\rm scf}$(gas) is the gas-phase SCF energy. In practice, it takes no more than one or two cycles to reach self-consistency.

The atomic excitation energies are calculated using the self-consistent ground-state crystal structure and atomic wave functions. The excited-state interaction potentials are found by treating the excited atom as an impurity in the ground-state atom host. The total electronic density is computed by replacing the ground-state atom at the origin with an excited-state atom in Eq. (1) and then subtracting that density in Eq. (7). Here, we consider only absorption and do not allow for relaxation of the lattice around the excited atom. The calculations are iterated, with the host fixed, until a self-consistent potential is found. The excitation energy is the difference in energy between the ground and excited states.

IV. RESULTS

A. Ground-state properties

The solid curve in Fig. 1 is the calculated pressure-volume curve for fcc Ar found using the gas-phase electronic density and dispersion coefficient. Also shown are the experimental results.[25,26] The theoretical curve is softer than the experimental curve, due primarily to neglect of the many-body dispersion interactions. Table I gives the experimental zero-pressure lattice parameters as well as the theoretical values calculated with the gas-phase atomic wave function. Considering the neglect of lattice motions and many-body contributions to the dispersion energy, the disagreement with the experiment is small (within 2% in lattice parameter). Using the estimates of Aziz[24] for the zero-point energy (0.000 297 hartrees) and many-body contributions to the dispersion energy (0.000 083 hartrees), our calculated lattice energy for Ar at 0 K and zero pressure deviates by only 3% from the experimental value. Also given in Table I are the lattice parameters calculated with the gas-phase atomic wave function at higher pressures. With the use of these lattice parameters, the crystal potentials [Eqs. (7) and (8)] for Ar at a series of pressures were generated. An example of the

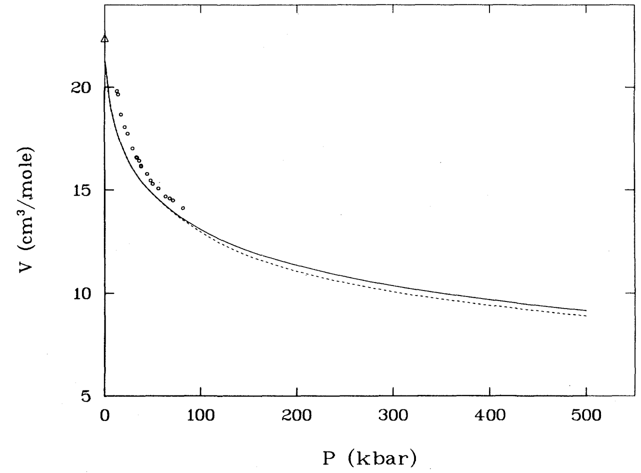

FIG. 1. Pressure-volume curve for solid Ar. Solid curve is the theoretical curve found with gas-phase atoms and dashed curve is the self-consistent curve. Diamond at zero pressure is the low-temperature experimental value of Ref. 25, and solid circles are the experimental points of Ref. 26 at room temperature.

TABLE I. Calculated crystal properties for solid Ar. P is the pressure in kbar, a is the nearest-neighbor distance in bohr, G' is the calculated lattice free energy $G' = E_l + PV$, E_s is the atomic stabilization energy of Eq. (8), and G is the total free energy $G' + E_s$. Energies are given in hartrees.

P	a	G'	E_s	G
Experiment[a]	7.08			−0.0029
0[b]	6.96	−0.0034		−0.0034
0[c]	6.96	−0.0034	0.0000	−0.0034
0[d]	6.96			−0.0030
100[b]	5.92	0.0549		0.0549
100[c]	5.90	0.0532	0.0009	0.0541
200[b]	5.65	0.1009		0.1009
200[c]	5.60	0.0971	0.0022	0.0993
300[b]	5.48	0.1421		0.1421
300[c]	5.42	0.1362	0.0035	0.1396
500[b]	5.25	0.2160		0.2160
500[c]	5.20	0.2057	0.0062	0.2119

[a] Reference 25 at 4.2 K and atmospheric pressure.
[b] Calculated with gas-phase atoms.
[c] Self-consistent crystal calculation.
[d] Energy including zero-point energy and many-body dispersion energy from Ref. 13.

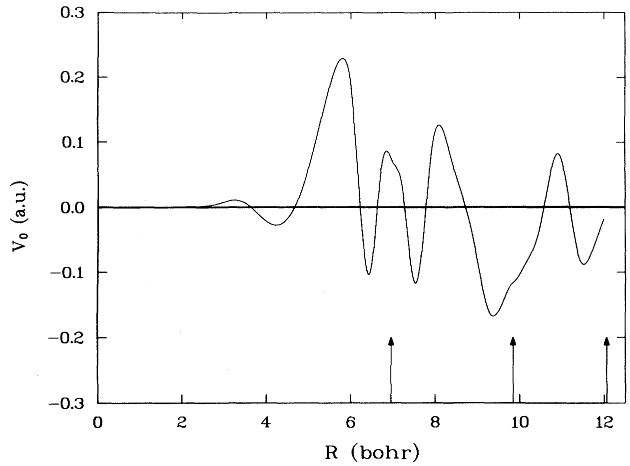

FIG. 2. Ar self-consistent crystal potential V_0 at zero pressure as a function of the distance from the atomic nucleus R. Arrows on the R axis are the neighbor-shell positions.

crystal potential at zero pressure is given in Fig. 2, where the positions of the neighbor shells are shown. The complicated shape is due to the balance between the repulsive forces and the attractive electrostatic forces. As noted earlier, only the first shell makes a major contribution to the perturbation integrals for the ground-state atom. As the pressure is increased, the shells move closer in and the crystal potential becomes more repulsive.

In Table I are given the lattice parameters calculated with the self-consistent crystal atomic wave functions. At zero pressure, the atoms are essentially unperturbed from their gas-phase state, and the self-consistent structure and energy are the same as that found with the gas-phase atoms. As the pressure is increased, the lattice parameter found with the crystal atomic wave function becomes smaller than that found with the gas-phase wave function. By 500 kbar, the lattice parameter has been reduced by about 1% from the gas-phase atom calculation, giving a volume difference of about 3% and an energy difference of about 2%. The change in the atomic electronic distributions can be seen in Fig. 3, where the crystal atomic density is plotted and compared with that for the gas-phase atom. As the pressure is increased, the electrons of the atom are compressed to a smaller volume. The driving force for this compression is the reduction in total free energy due to the smaller lattice. There is a balance between this energy gain and the energy necessary to compress the atom. At 500 kbar, about 0.01 hartree are gained by having the smaller atoms in the lattice, but 0.006 hartree are needed to perturb the atoms (E_s in Table I). The dashed line in Fig. 1 is the self-consistent pressure-volume relation for Ar. The smaller volumes found with the crystal atomic wave functions indicate that the effective interaction in the solid is less repulsive than that between gas-phase atoms.

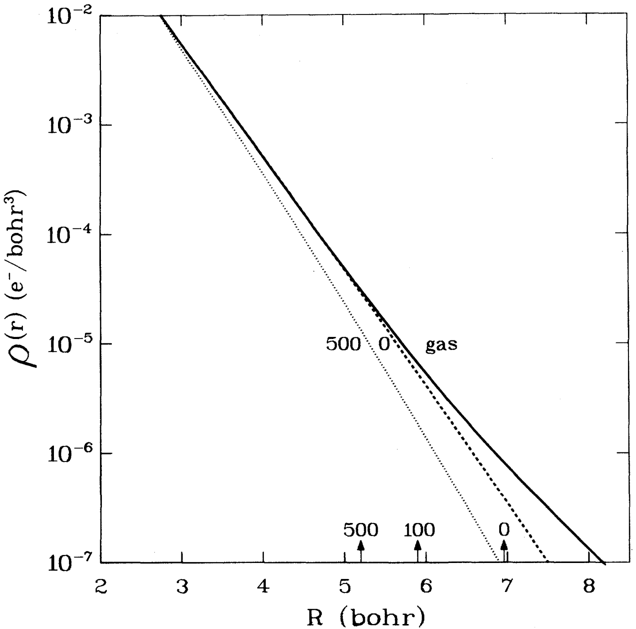

FIG. 3. Logarithm of the electronic density $\rho(r)$ of the atoms as a function of distance R from the nucleus and of pressure. Given are the gas-phase, zero-pressure, and 500-kbar atomic densities. Marked along the R axis are the nearest-neighbor positions for the 0-, 100-, and 500-kbar crystals.

In Table II we show how the orbital energies change with pressure. There is a gradual positive shift in energy as the pressure is increased, with a change of almost 7% relative to the gas-phase value in the energy of the outermost orbital ($3p$) by 500 kbar. The inner orbitals are much less affected by the crystal potential, with the $2p$ orbital shifted by only 0.6% at 500 kbar. The shifts, while small, indicate a perturbation of the electronic structure of the inner shells. One other measure of this perturbation can be found by examining changes in the electronic density of the individual orbitals. We find for Ar at 500 kbar essentially no changes (less than 5%) in the $2s$ and $2p$ electronic distributions from the gas-phase values until a distance of about 2 bohr from the nucleus, where the contribution from these orbitals to the atomic electronic density is about 10^{-6} $e^-/$ bohr^3 out of a total density of about 0.05 $e^-/$ bohr^3.

As the atoms are compressed in the crystal lattice the extent of their electronic distributions is decreased (Fig. 3). The change of $(\langle r^2 \rangle)^{1/2}$ with pressure is given in Table III. There is a 3% decrease in the radius of the distribution from the gas-phase value to that found in the 500-kbar crystal. By using Eqs. (2) and (3) we find the values for the polarizability and dispersion constant shown in Table III. We see that the atomic polarizability decreased by about 9% up to 500 kbar, while the effective dispersion constant is reduced by 13%. Because of the crude nature of the Kirkwood formula, the polarizability changes should be considered as only qualitative measures of the effects of compression. The decrease in the dispersion contants makes the interatomic interaction potential less attractive. If the gas-phase dispersion term had been used in the calculation of the self-consistent crystal structure, then the effects of pressure on the interaction energy would be greater, yielding a slightly softer pressure-volume curve.

TABLE II. Orbital energies of Ar under pressure. Orbital energies for the gas-phase atom are given in hartrees in column 1, with changes in eV relative to the gas-phase values given as a function of pressure in kbar in the other columns.

Orbital	Gas	$P=0$	100	200	300	500
1*s*	−118.6104	0.038	0.5604	0.999	1.301	1.815
2*s*	−12.3222	0.035	0.547	0.901	1.167	1.625
2*p*	−9.5715	0.035	0.550	0.906	1.173	1.633
3*s*	−1.2774	0.027	0.365	0.574	0.743	1.039
3*p*	−0.5910	0.028	0.365	0.610	0.798	1.128
$E_{\mathrm{scf}}^{\mathrm{a}}$	−526.8171	−526.8154	−526.7900	−526.7685	−526.7508	−526.7151

[a] SCF energy including interaction with potential.

B. Excited-state properties

The crystal potentials for the Ar ^1P and ^3P states (electron configuration $1s^2 2s^2 2p^6 3p^5 4s^1$) were found using the self-consistent ground-state atomic densities and lattice constants. The reference potential H_m in Eq. (7) was that of the excited atom, assuming spherical densities. Because of the large radial extent of the excited-state electronic distributions, it was necessary to include a large number of neighbor shells in the calculation of the perturbation integrals. For $P=0$, three neighbor shells were needed, but for $P \geq 100$ kbar, a revised procedure was found to be necessary. Our original procedure had been to calculate the crystal potential to some distance, $r_{\max}$, from the nucleus of the excited-state atom. We discovered, however, that in the optimization of the 4*s* orbitals, a spurious energy minimum can be found with appreciable electronic density in the region where the potential is set to zero ($r > r_{\max}$), thus giving a solution with a delocalized wave function. Since it is cost prohibitive to carry out the calculation of the potential to very long distances, we approximated the potential beyond $r_{\max}$, set to include six or seven shells, by a constant that is roughly the average of the potential in the shells with $r < r_{\max}$. The optimized wave functions found with this potential exhibit localized electronic densities (going exponentially to zero with distance). To ensure that errors are not introduced by the constant potential, the optimized basis set is used to calculate the energy of the excited-state atom with the potential set to zero for $r > r_{\max}$. For all cases studied, the energy differences between the wave functions calculated with the constant potential and the zero potential were less than 0.01 eV.

The Slater open-shell interaction parameters were used to calculate the excited-state energies.[21] Excitation energies were found by subtracting the ground-state SCF energy of the atom, including the interaction with the crystal field, from the energy of the state with an electron promoted to the 4*s* orbital. The results are shown in Fig. 4. Comparison of the excitation energies calculated for gas-phase Ar atoms with the experimental values[27] (Fig. 4) shows that the SCF method underestimates the energy change by about 0.7 eV for both the ^3P and ^1P states. This error is due to a lack of correlation in the Hartree-Fock method, where inclusion of the correlational energy would

TABLE III. Variation of atomic properties with pressure. Pressure P is in kbar and the electronic radius $(\langle r^2 \rangle)^{1/2}$, the polarizability $\alpha(P)$, and the dispersion coefficient $C_6(P)$ are all in a.u. Gas-phase polarizability is α_g.

P	$(\langle r^2 \rangle_p)^{1/2}$	$\alpha(P)$	$\alpha(P)/\alpha_g$	$C_6(P)$
Gas	5.102[a]	11.091[b]	1.000	64.8[b]
0	5.097	11.044	0.996	64.4
100	5.055	10.687	0.964	61.3
200	5.030	10.471	0.944	59.4
300	5.014	10.343	0.933	58.4
500	4.957	10.122	0.913	56.5

[a] Calculated from the gas-phase SCF wave function.
[b] Reference 24.

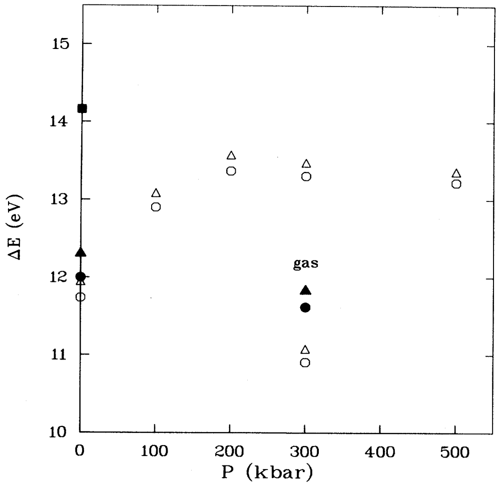

FIG. 4. Exciton energies ΔE as a function of pressure for Ar. Open symbols are those from theoretical calculations with the results for the ^3P excitations given as circles and for the ^1P excitations given as triangles. Closed symbols are the experimental results. Band gap (closed square) is from Ref. 29 and the exciton energies at zero pressure are from Ref. 28. Also given are the experimental (from Ref. 27) and theoretical (present) gas-phase excitation energies.

lower the electronic energy of the ground state more than it would the more diffuse excited states. The present results are in better agreement with the experimental exciton energies for the zero-pressure solid[28] (Fig. 4), with error in the ^3P exciton of about 0.3 eV (19 mRy) and that for the ^1P of about 0.4 eV (26 mRy). The shifts in the excitation energies upon going from the gas to the solid are overestimated in the present model by roughly a factor of 2 due to the large error in the gas-phase values. As the pressure is increased we see a gradual increase in the exciton energies to 200 kbar, and then a slight decrease, with a shift at 500 kbar of about 1.5 eV from the zero-pressure value for both the triplet and singlet excitons. The zero-pressure experimental band gap at 14.16 eV is shown in Fig. 4.[29] Since band-structure calculations give a value for the gap ranging from 8.3 to 18.5 eV, depending on the scheme used,[30] we do not plot the calculated pressure-dependent band gap.

V. DISCUSSION

The model used here is based on the view that for closed-shell molecular crystals, the crystal properties are determined mainly by the ground-state properties of the molecules (rare-gas atoms). This view places limitations on the validity of the model, such that we must restrict its application to regimes where the electrons are tightly bound to their molecular site. Thus the crystal must be far from the onset of metallization, where long-range fluctuations of the electrons may occur. For Ar, the metallization pressure is estimated[31] to be about 5.8 Mbar, so we believe the present application is valid.

A measure of the validity of the tight-binding approximation is the width of the valence band. Here we assume that atomic states are good approximations to states in the crystal, which applies only if the bands are narrow. Band-structure calculations estimate the zero-pressure $3p$ bandwidth to be about 0.6—1.7 eV, with an orbital energy of about -15.8 to -17.4 eV.[30] The narrowness of the bands supports the view of the localized nature of the bonding.

One aspect of the present model that is somewhat different from the usual calculations of the electronic structure of solids is the mixture of local-density functionals and Hartree-Fock theory. The difficulties with the SCF method, as applied here, are the use of nonrelativistic wave functions and the lack of electron correlation. Although relativistic corrections are not important for Ar,[32] they may be for materials such as Xe. The neglect of electron correlation, however, causes appreciable error in the total electronic energy of the molecules and in the long-range electronic distributions. Inclusion of the correlation energy is difficult in the SCF formalism unless very complicated and expensive configurational interaction calculations are employed. Use of a density-functional method that includes a correlational term (Kohn-Sham[33]) for calculation of the atomic states may improve the present results.

One other problem with the treatment of the correlation energy is the simple electron-gas expression we used in defining the crystal potential [Eq. (5)]. Recent developments in the theory of correlation energies in the non-local-density approximation may provide a better correlational energy than the expression used.[34] However, the neglect of long-range interactions with the fluctuating electrons is probably the more serious error. To treat these interactions properly would require the use of linear-response theory, which we have not considered.

In spite of the approximations used in the present model, the results are interesting and quite reasonable. The compression of the atoms at high pressure implies that crystal structures calculated with gas-phase interaction potentials would have larger volumes at high pressures than those found experimentally. Unfortunately, by neglecting the many-body dispersion interactions, we find the pressure-volume relation calculated with gas-phase atoms to be softer than experiment, and with the self-consistent results even softer, definitive comparisions are impossible. This apparent softening of the interaction potential at high pressure has also been noticed by others calculating high-pressure equations of state.[35] The change in dispersion energy coefficients with pressure (13% at 500 kbar) will have some effect on the calculated crystal parameters. However, neglect of many-body forces and the higher terms in the dispersion-energy expansion, coupled with a breakdown in the expansion at small distances, may cause much larger errors than those induced by not including changes in the C_6 coefficient.

In Table II we show how the orbital energies change with pressure. The perturbation of the inner cores is small, as discussed relative to changes in the electronic distributions. The lack of changes in the inner electrons indicates that pseudopotential methods, which depend on freezing the cores at their gas-phase values, can be used for Ar with little error, at least to 500 kbar. If the inner orbitals become more perturbed, as the pressure is increased further, then it will be necessary to consider them "unfrozen."

We show how the atomic polarizabilities change in Table III. As the pressure is increased and the atoms are compressed, there is a gradual reduction of the polarizability, until at 500 kbar, the decrease is 9%. Although there are no experimental data, we can compare our results to those found by ten Seldam and de Groot[35] in a calculation of an Ar atom in a rigid spheroidal box. Using the rigid walls of the box as a model of the high-pressure crystal environment, they found an 8% decrease in the polarizability at about 3 kbar. While the box model greatly exaggerates the effects of pressure, it gives qualitatively correct results for a number of atomic and molecular properties.[37] The present results may provide a way of rescaling the pressures in a simple box calculation. The calculated reduction in the polarizability with pressure also may be used to refine the predictions of the Herzfeld criteria for metallization,[31,38] which predicts the metallic transition when the molar volume of the solid is proportional to the polarizability.

One of the most difficult problems in solid-state physics is the calculation of electronic excitation energies. Local-density-functional methods have not been very successful in calculating excitation energies and band gaps for insulating systems. Despite the interest in calculating excitation energies, only a few calculations are available, mostly on the inert gases.[39] Probably the most successful calculation on the zero-pressure Ar crystal was by Andreoni *et al.*[40] who obtained a result within 0.03 eV (2 mRy) of the experimental value. Their method depended on the truncation of a sum over the terms in the crystal Green function at the nearest neighbors and an accurate value for the band gap; therefore, they cannot be used at higher pressures unless the pressure-dependent band gap is known and more neighbors are included, greatly increasing the time of the calculation. We find much less compression of the excited-state wave function in the first-neighbor sphere than did Andreoni *et al.*,[40] and at distances far beyond the first shell, the crystal excited-state wave function is more diffuse than the gas-phase excited-state wave function. The greater diffuseness of the wave function may be why we needed to consider more interaction shells than did Andreoni *et al.*,[40] even at zero pressure.

Considering the simplicity of the model and the inaccuracies of the Hartree-Fock method, the present method does very well (within 2.5%) in the calculation of the solid-state excitation energies. As shown in Fig. 4, the Hartree-Fock method greatly underestimates the excitation energies in gas-phase atoms, while the CP model does much better in the solid. Because of the hybrid nature of the method, which employs an uncorrelated calculation of the atomic properties and includes some correlation in the interaction potential, it is difficult to locate the features in our model that give a better description of the solid than the Hartree-Fock method does for the gas. It may be that the correlational interaction energy is more important for the more diffuse excited state than the ground state, and that the total error in correlational energy is then about the same for both states. If that is the case, the difference between the energies of the two states (the excitation energy) might be determined with reasonable accuracy. This idea is supported by a somewhat similar method,[41] proposed a few years ago for finding energy changes in impurity atoms, which did not include correlation energy at all and had similar accuracy as the present study. When other systems have been studied with the present model it may be possible to offer a more definite answer.

As the pressure is increased, the excitons in the solid shift to higher energy, with a shift of about 1.6 eV from zero pressure to 200 kbar at first. These results are quite similar to those from calculations done with a Hartree relaxation model on solid Ne, where the authors[42] found about a 0.5-eV shift in the excition from 0 to 20 kbar. As the pressure is increased, the band gap should close. Because of uncertainty in the band-structure calculations at large volumes, it is difficult to predict exactly where the excitions would be cut off by the descending band edge.

To test the model further, we are presently considering a case where the applicability of the tight-binding approximation may be less valid, namely that for solid Xe. We shall examine how the model behaves on approach to metallization. We shall also consider combining the present model with a "Wigner-Seitz" calculation,[43] or with the method suggested by Anderson[44] to develop a unified scheme allowing calculation of both local and band properties.

VI. SUMMARY AND CONCLUSIONS

We have presented a simple model for examining perturbations of the electronic structure of molecular and rare-gas crystals. By focusing on the local site properties we have been able to examine changes in both ground- and excited-state properties of solid Ar as a function of pressure. We find that the atoms compress with pressure, due to the gain in free energy caused by a similar lattice. Self-consistency is reached when this gain in free energy is balanced by the energy required to compress the atoms. Because many-body dispersion interactions are neglected, the calculated pressure-volume curve is too soft. Excited-state properties are easily calculated and agree properly with the experiment. It is possible to extend the present simple methods to much more complicated systems.

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