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Self-consistent pseudopotential method for localized configurations: Molecules*

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A method is proposed using pseudopotentials in a self-consistent manner to describe localized configurations such as molecules, surfaces, impurities, vacancies, finite chains of atoms, adsorbates, and solid interfaces. Specific application is made to the Si_2 molecule. The Si_2 energy levels and charge densities are calculated with reasonable accuracy using a plane-wave basis set.

We have developed a method which extends the pseudopotential scheme to localized configurations. These calculations are done self-consistently and the approach is applicable to problems such as atomic and molecular states, solid surfaces,[1] localized impurity and vacancy states,[2] finite chains or layers, adsorbates,[3] and interfaces between solids.[4] The scheme has many of the advantages of the pseudopotential method in that it uses a simple plane-wave expansion and the starting potential can be obtained from experimental data. It goes beyond the usual pseudopotential approach through the requirement of self-consistency for the valence electrons. Here we treat the case of a silicon diatomic molecule both to illustrate the method and to demonstrate the interesting results which are possible for molecular calculations. Hopefully this approach can become competitive with other approximate one-electron schemes based on methods such as multiple scattering $X\alpha$, extended Hückel, tight binding, etc.

For calculations of molecular states, the main advantage of our method over many standard methods (essentially embodied in the pseudopotential method) is that the properties of the core electrons need not be computed. Consequently, calculations for the heavier molecules are no more difficult than for light ones, within the "frozen-core" approximation. For light molecules, standard methods are very successful, but because the computation time increases rapidly with the number of electrons, there is a paucity of calculations for molecules composed of atoms beyond the first transition series. The simplicity of the proposed pseudopotential scheme also allows calculations for larger molecules. At first sight the plane-wave basis set used appears to be retrogressive, but there are in fact advantages to this approach. Because of the plane-wave basis and the use of statistical exchange (discussed later), there is no *a priori* bias as to the form of the wave function—its form is determined self-consistently via the potential. Also because we are using a pseudopotential approach, only the valence-electron charge density is computed, and the basis set need only be large enough to reproduce variations in this fairly smooth pseudocharge distribution. Specifically, the charge variation away from the cores is not large and hence the plane-wave basis set and resulting matrix are easily handled by modern computers. The properties and problems associated with *d* electrons are not included here. However, there appears to be no fundamental restriction in the model which rules out application to *d* states. In particular, several empirical-pseudopotential methods involving *d* states have been developed[5] and applied successfully to band-structure calculations for crystals. We will first discuss the method in general and then return to the molecular calculation.

Pseudopotential methods have evolved considerably since their introduction[6] in 1959. The use of model potentials[7] and the empirical-pseudopotential method[5] (EPM) have yielded a great deal of information about solid state properties such as band structure, optical response functions and electronic charge densities.[8] In all of these cases the sytems considered were assumed infinite and periodic; and possible extensions of the method to local configurations in solids, e.g., localized impurities or solids without long-range periodicity were not obvious. An attempt[9] was made to use the pseudopotential scheme to study amorphous materials. Complex cells were repeated infinitely and the effects of the complexity of the unit cells on the calculated properties yielded information about how the prominent features of the structure (e.g., even and odd numbered rings of bonds) influenced the properties (e.g., electronic density of states). A true amorphous system was not generated, but information gained from studies of increasingly complex cells was extremely useful.

The method discussed here is somewhat related to the above scheme, and it is directly applicable to the specific problem of interest. The method is straighforward and initially involves putting the local configuration of interest into the structure factor. In the pseudopotential formulation, the crystalline pseudopotential form factors $V(\vec{G})$ are written in terms of atomic potential form factors $V_a(\vec{G})$ through the structure factor $S(\vec{G})$,

$$V(\vec{G}) = \sum_{\tau_a} S(\vec{G}) V_a(\vec{G}), \qquad S(\vec{G}) = e^{i\vec{G}\cdot\vec{\tau}_a}, \tag{1}$$

where $\vec{G}$ is a reciprocal-lattice vector and τ_a are the basis vectors to the various atoms in a primitive cell. The basic scheme is to include in $S(\vec{G})$ the essential features of the local configuration. In the case of a molecule, the structure factor can be constructed to create a cell with a molecule and sufficient empty space around the molecule to provide isolation from the next molecule when the cell is repeated. For a surface, usual periodicity can be retained in two dimensions and a slab can be inserted to provide a surface in the third dimension. The impurity or vacancy problem requires a cluster of host atoms surrounding the site of interest. Ultimately the cell chosen is repeated indefinitely to allow the use of the pseudopotential method. A similar approach specifically designed for surfaces has been used by Alldredge and Kleinman[10] to calculate some properties of Al and Li surfaces.

Self-consistency[11] is essential in obtaining realistic solutions since the calculations will start with potentials derived for bulk calculations. It is necessary to allow the valence electrons to react to the boundary conditions imposed by the local configuration and the resulting readjustment and screening is a fundamental part of the problem. Also, the self-consistent screening potential has to be completely general and is not necessarily a superposition of atomic potentials. Self-consistency is restricted to the valence electron since a fixed ion core pseudopotential is used. Changes in the core electrons due to feedback from valence electrons are neglected since they are usually localized in a limited region around the ion cores and not significant for determining the valence-electron and bonding properties of the system.

In the scheme described above, the configuration of atoms and spaces can be complex. The ultimate limitation on the number of atoms is the amount of computer time necessary to generate the eigenvalues and eigenfunctions through solution of the secular equation. The basis set is formed by Bloch waves expanded in terms of free-electron eigenfunctions.

The starting potential can be an ionic model potential fit to atomic term values and screened appropriately or a potential obtained from measurements on bulk solid-state properties. In both cases the results are the same once self-consistency is reached. The problems with the method come mainly via the artificial long-ranged symmetry imposed, but most of the consequences can be dealt with. Some examples are: the interaction between configurations; establishing a zero of energy; the fact that the potential which should depend continuously on wave vector q is approximated by form factors at $\vec{q}$'s equal to the $\vec{G}$'s of the chosen lattice structure; and the symmetry of the configuration to some extent suggests the choice of lattices. Most of the above potential problems are eliminated or reduced by taking large enough cells and cells of the appropriate structure or symmetry. In the diatomic molecule case which has $D_{\infty h}$ symmetry, the most convenient lattice structure is hexagonal with D_{6h} symmetry. Thus the ∞ rotational symmetry of the wave function is simulated by sets of sixfold "stars" of plane waves. Test calculations on the Si_2 molecule in a trigonal lattice with D_{3d} symmetry show that the self-consistent results are weakly dependent on the chosen "crystal structure" provided convergence is reached, i.e., enough plane waves are taken into account.

The Si_2 molecule calculation was done in the following way. The molecule was placed in a hexagonal lattice with a c/a ratio chosen such that the distance between any two atoms not belonging to the same molecule was larger than three bond lengths. The molecule bond length was taken from experiment to be 2.25 Å in the ground state[12] which differs considerably from the 2.34 Å for the Si crystal. The wave function was expanded in about 180 plane waves including 250 more plane waves by a second-order perturbation scheme.[5] The first step in the self-consistent calculation was performed using the superposition of two atomic potentials taken from empirical crystal calculations. A continuous curve[5] of the form

$$V(q) = a_1(q^2 - a_2)/\{\exp[a_3(q^2 - a_4)] + 1\} \tag{2}$$

was fit to the few crystalline form factor values to provide potential values at the new "molecule $\vec{G}$ vectors." The dispersion of the eigenvalues in $\vec{k}$ space which is a measure of the interaction of the different molecules with each other was of the order of 0.8 eV at this stage; it decreased to about 0.2 eV in the course of self-consistency. From this starting calculation the total charge $\rho(\vec{r})$ was evaluated in terms of its Fourier components $\rho(\vec{G})$ and a Hartree-like screening potential

$$V_H(\vec{G}) = 4\pi e^2 \rho(\vec{G})/\Omega_c |\vec{G}|^2, \tag{3}$$

defined by

$$\Delta V_H(\vec{r}) = -4\pi e^2 \rho(\vec{r}) \tag{4}$$

as well as an exchange potential given by

$$V_x(\vec{r}) = -\alpha(3/2\pi)(3\pi^2)^{1/3}e^2\rho(\vec{r})^{1/3}, \tag{5}$$

with $\alpha = 0.79$ were computed. The use of a statistical exchange of the above form for atoms, molecules, and solids has been discussed widely in the literature[13] and been proven to yield satisfactory results. The calculation of $V_x(\vec{r})$ requires knowledge of the function $[\rho(\vec{r})]^{1/3}$. For this purpose $\rho(\vec{r})$ was evaluated on a grid of points (~10 000 per unit cell), the cube root was taken at each grid point and the result was transformed back into a Fourier series resulting in $V_x(\vec{G})$. The sum of these potentials was added to a bare ion pseudopotential obtained from empirical atomic calculations.[7] The local "on the Fermi sphere" approximation to this originally nonlocal potential was used and a continuous curve of the form

$$V_{\text{ion}}(q) = \frac{a_1}{q^2}\left[\cos(a_2 q) + a_3\right]e^{a_4 q^4} \tag{6}$$

was fit to the results. Support for the use of this atomic ionic potential in the molecular case is also obtained from the fact that if this potential is used in a self-consistent band-structure calculation for the crystal, excellent results are obtained. The quality of these calculations can be further improved if the ionic potentials are constrained to give accurate atomic wave functions in addition to accurate energy levels.

The computational procedure was then continued until self-consistency was reached. The process of reaching self-consistency can be speeded up by interpolating appropriately between output and input potentials for consecutive steps. We thus needed five steps to reach self-consistency of the eigenvalues to within 0.05 eV. The resulting potentials $V_{\text{ion}}(\vec{r})$, $V_H(\vec{r})$, and $V_x(\vec{r})$ are plotted in Fig. 1 along the line, connecting the two Si atoms. The total self-consistent potential is also shown and compared to the *empirical* input potential which gives the best description of Si atoms in the crystalline phase. The interesting results are that (a) the Hartree screening potential is essentially featureless, (b) the exchange potential is comparable in strength to the total self-consistent potential, and (c) the total self-consistent potential is considerably deeper at the bond than the empirical starting potential. Also indicated in Fig. 1 are the occupied molecular one-electron energy levels σ_S at -1.0 Ry, σ_S^* at -0.64 Ry, σ_p at -0.39 Ry, and π_p at -0.38 Ry.

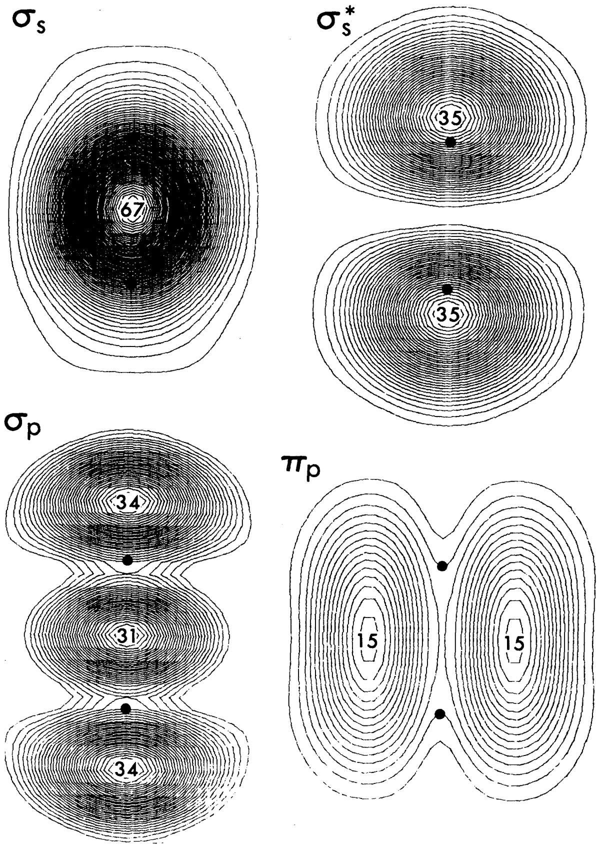

FIG. 2. Charge-density contours for the four occupied molecular orbitals. The values are given in $2e/\Omega_c$, where $\Omega_c = 400$ Å^3 is the unit-cell volume.

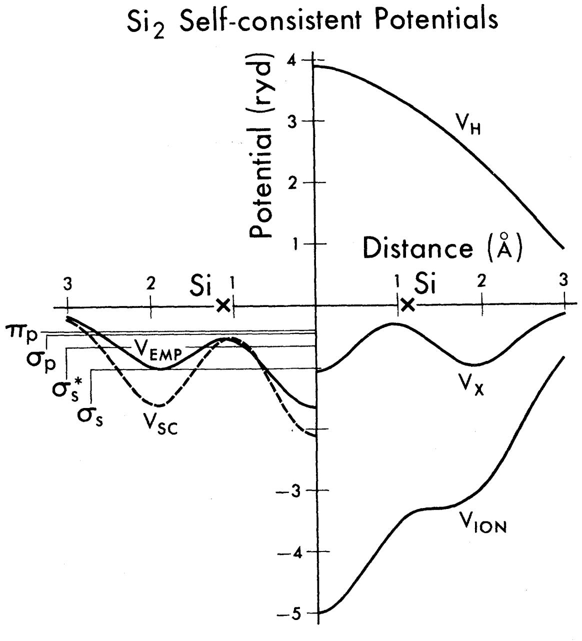

FIG. 1. Molecular potentials plotted along a line connecting the two Si atoms. Also indicated are the molecular-orbital energies.

In Fig. 2 we display charge density contours for the four occupied molecular levels. The charge density values are given in $2e/\Omega_c$, where $\Omega_c = 400$ Å^3 is the unit-cell volume. It should be emphasized

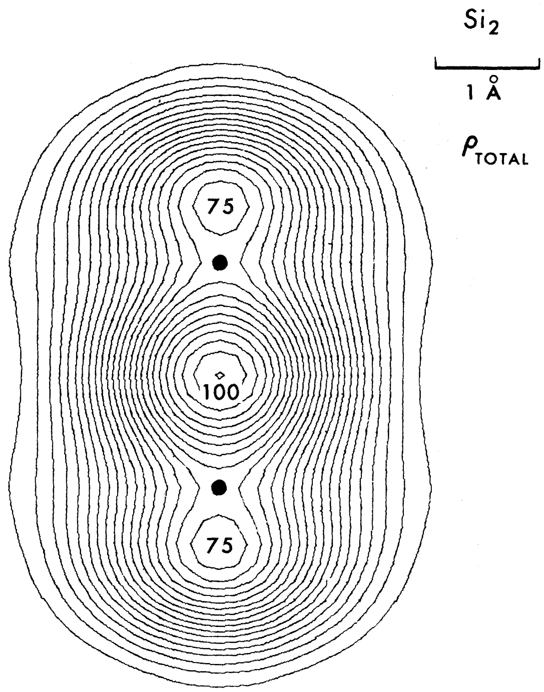

FIG. 3. Total charge density of the Si$_2$ molecule in the ground state.

at this point that these textbooklike molecular densities were calculated using a plane wave basis. The lowest level σ_S contains mostly s-like charge in a bondinglike configuration with its maximum between the two atoms. The next higher level σ_S^* has antibonding s-like character. Some admixture of p states quantized along the molecular axis is present. The wave functions of the third occupied level are predominantly p-like at the two atoms and overlap forming a σ-type bonding state. The fourth (occupied) and fifth (empty) level are "quasidegenerate." The wave functions are mostly p-like in character and form π-type bonding states. The σ_p^* and π_p^* antibonding levels lie at higher energies and are unoccupied. Experimentally,[12] the ground state is found to be a Σ triplet which is reproduced in our model assuming triplet coupling of the π electrons (Hund's rule). The inclusion of spin-dependent correlation potentials would be necessary to *a priori* distinguish between singlet and triplet states. The total charge density corresponding to the four occupied levels is presented in Fig. 3; the units of the indicated values are the same as in Fig. 2. Comparison of the above orbital energies (after adjustments for the zero of energy) with results[14] using a Hartree-Fock basis yields good agreement. The Hartree-Fock calculation gives the π_p state slightly lower than σ_p and hence a singlet ground state. This probably results from the configuration choice.

To obtain an estimate for the amount of charge in the bond we proceed as in Ref. 8 and integrate the charge pile-up over a region defined by the outermost closed contour. This is just an approximate scheme to compute the charge in the band which depends on the topology of the charge configuration. For Si$_2$ a value of $Z_B = 0.138$ (in units of e) is obtained which is within computational accuracy identical to the crystalline value of $Z_B = 0.125$.

Concluding, we have introduced a method which is fairly simple to use and efficient; it offers a new tool for molecular calculations and establishes connections between a solid state method and molecular problems. Si$_2$ was chosen as a test case because of the detailed knowledge available for the Si pseudopotential. The results are satisfactory and they illustrate the potential of the method and the possible extensions. Hopefully our scheme can be amplified to give accurate values of equilibrium configurations, force constants and information about the geometry of molecular systems. At present we have concentrated on special properties. Force constants which are a more stringent test of the quality of the wave functions can be computed within the pseudopotential scheme.[15]

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