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A SOLID STATE APPROACH TO THE ELECTRONIC STRUCTURE OF MOLECULES: SELF-CONSISTENT PSEUDOPOTENTIAL CALCULATION OF O_2

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A first principles non-local pseudopotential method is used to solve the SCF equation for a molecule in the density functional approach. A superlattice technique is applied which allows an expansion of the molecular wavefunction in terms of a mixed basis set consisting of plane waves and localized orbitals. The efficiency of the method is demonstrated for the O_2 molecule.

A self-consistent pseudopotential method has recently been developed which allows the determination of non-local atomic pseudopotentials from first principles.[1] The basic idea of the method consists in solving Schrödinger's equation in the density functional formalism[2] for the outer valence electrons which move in an external potential that simulates the effect of the core electrons. This potential is completely determined if the following principles are applied. The valence pseudo wavefunctions are obtained from the all electron wavefunctions by a unitary transformation which is fixed by requiring that the pseudo orbitals are smooth and nodeless functions and match the all electron orbitals outside the core region. The resulting pseudopotentials yield very accurate energy eigenvalues, total energy differences and wavefunction moments over a wide range of excited atomic configurations.[1] Their weak energy dependence makes them useful for more complicated systems like molecules and solids. In contrast to conventional all electron methods like Hartree-Fock and LCAO-X_α the pseudopotential eigenvalue problem is considerably easier to handle, since core electrons do no longer occur explicitly. Furthermore, because core orthogonalization is simulated by a potential there is no need to calculate matrix-elements between core and valence states as done in frozen core methods.[3]

Here we present results for the electronic structure of the O_2 molecule. Although the isolated molecule can equally well be treated by conventional techniques, this approach provides a useful test case for the efficiency of our method.

To use standard band structure techniques the molecule is placed into a periodic lattice. The periodically repeated molecules are sufficiently separated from each other (at least 3.6 Å) such that mutual interactions are practically zero. The "band-structure" of this superlattice is calculated from a one particle pseudopotential Hamiltonian

$$H = p^2/2m + V_{ps} + V_{coul} + V_{XC} \quad . \tag{1}$$

V_{coul} is the usual electronic Coulomb potential which is obtained from the total pseudopotential charge density $\rho(\vec{r})$ by solving Poisson's equation. The exchange-correlation potential V_{XC} is given in the local density approximation to lowest order by Slater's[4] $\rho^{1/3}$ term

$$V_X(\vec{r}) = -\frac{3\alpha}{2} e^2 \left(\frac{3}{\pi}\right)^{1/3} \rho^{1/3} \quad . \tag{2}$$

We used the Kohn-Sham-Gaspard value[2] of $\alpha=2/3$ which has been shown to give excellent agreement with experimental binding energies of molecules.[5]

Assuming that the atomic 1s state of the oxygen does not contribute much to the molecular binding we describe its effect on the remaining 2s and 2p electrons by a superposition of nonlocal core pseudopotentials

$$V_{ps}(\vec{r},\vec{r}') = \sum_{R_n} v_{ps}(\vec{r}-\vec{R}_n, \vec{r}'-\vec{R}_n) \quad . \tag{3}$$

v_{ps} is obtained by the first principle pseudopotential method described in Ref. 1 and is decomposed into s- and p-potentials which act on the corresponding angular momentum components of the wavefunction separately e.g.,

$$v_{ps} \simeq \sum_{\ell=0}^{1} v_\ell P_\ell \quad , \tag{4}$$

where P is an angular momentum projection

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operator$^{\ell}$. Components of higher angular momenta are neglected, since the corresponding wavefunction components are considered to be small in the energy range of interest. The potentials $v_s(r)$ and $v_p(r)$ are shown in Fig. 1. Whereas the 2s electrons see a highly repulsive core due to the presence of the 1s electrons, the 2p electrons experience the full all electron atomic potential which is always attractive. Note that the centrifugal term is not included in these potentials.

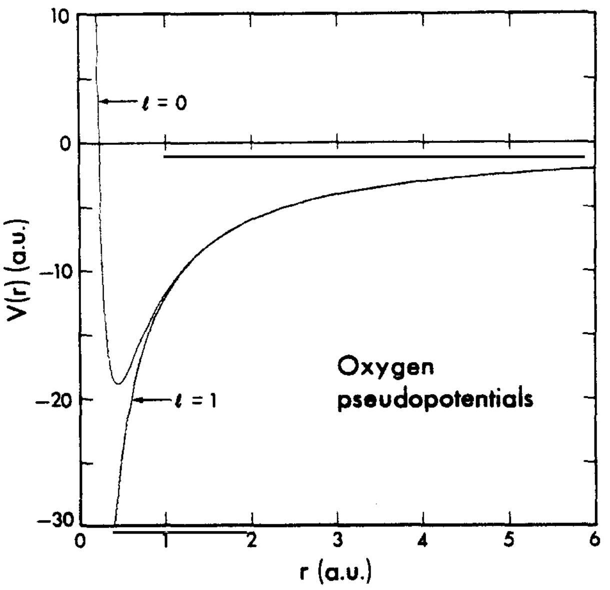

Fig. 1 First principles pseudopotentials for oxygen in real space.

The Schrödinger equation for the molecular Hamiltonian of Eq. 1 is solved self-consistently using a mixed set of plane waves and Bloch functions constructed from localized Gaussians.[6] This approach which has recently been used to calculate the bulk and surface properties of transition metals[7] takes into account the strong localization of the molecular wavefunction around the two oxygen atoms in the unit cell. A pure plane wave representation as used in Ref. 8 for the Si_2 molecule is inadequate for O_2 because of its strong wavefunction localization. The mixed basis approach requires one s- and one p-type Gaussian per atom and about 180 additional plane waves to obtain a satisfactory representation of the molecular wavefunctions.

The results for the molecular energy levels are listed in Table I. Very good agreement is obtained with the results of Baerends et al[3] who used a frozen core approximation within the Hartree-Fock-Slater (HFS) method and an exchange coefficient of $\alpha = 0.70$. The associated molecular charge densities for the various states are shown in Fig. 2 as contour plots. Also shown is the total valence charge density. All pseudopotential charge contour plots are compared with Hartree-Fock charge density contours given by Wahl.[9] Corresponding density functional charge densities have not been published yet. Except for the core regions which are defined by the spatial extent of the 1s wavefunctions, the pseudopotential charge density contours resemble closely the all electron charge densities.

Table I

Self-consistent eigenlevels for the O_2 molecule in eV and quoted with respect to the vacuum level. The superscript indicates the number of electrons occupying the molecular shell.

	present work	Ref. 3 HFS
$2\sigma_g^2$	-32.1	-32.1
$2\sigma_u^2$	-19.6	-18.0
$2\sigma_g^2$	-11.9	-12.0
$1\pi_u^4$	-10.8	-11.6
$1\pi_g^2$	- 3.3	- 4.7

In conclusion, we have shown that the superlattice technique[8] together with the self-consistent first principle pseudopotential method[1] is capable of describing the electronic structure of molecules. In the case of O_2 the highly localized nature of the molecular wavefunctions necessitates the use of localized orbitals[7] to complement the plane wave basis. No core states need to be included into the molecular eigenvalue problem. This allows the treatment of more complex molecules which are less accessible by other techniques. Due to its solid state character, the method is also readily applicable to systems in which molecules are in contact with solid surface i.e., chemisorption processes. The pseudopotential wavefunctions obtained by the present method can also be used to describe the spatial behavior of the all electron charge density outside the core regions.

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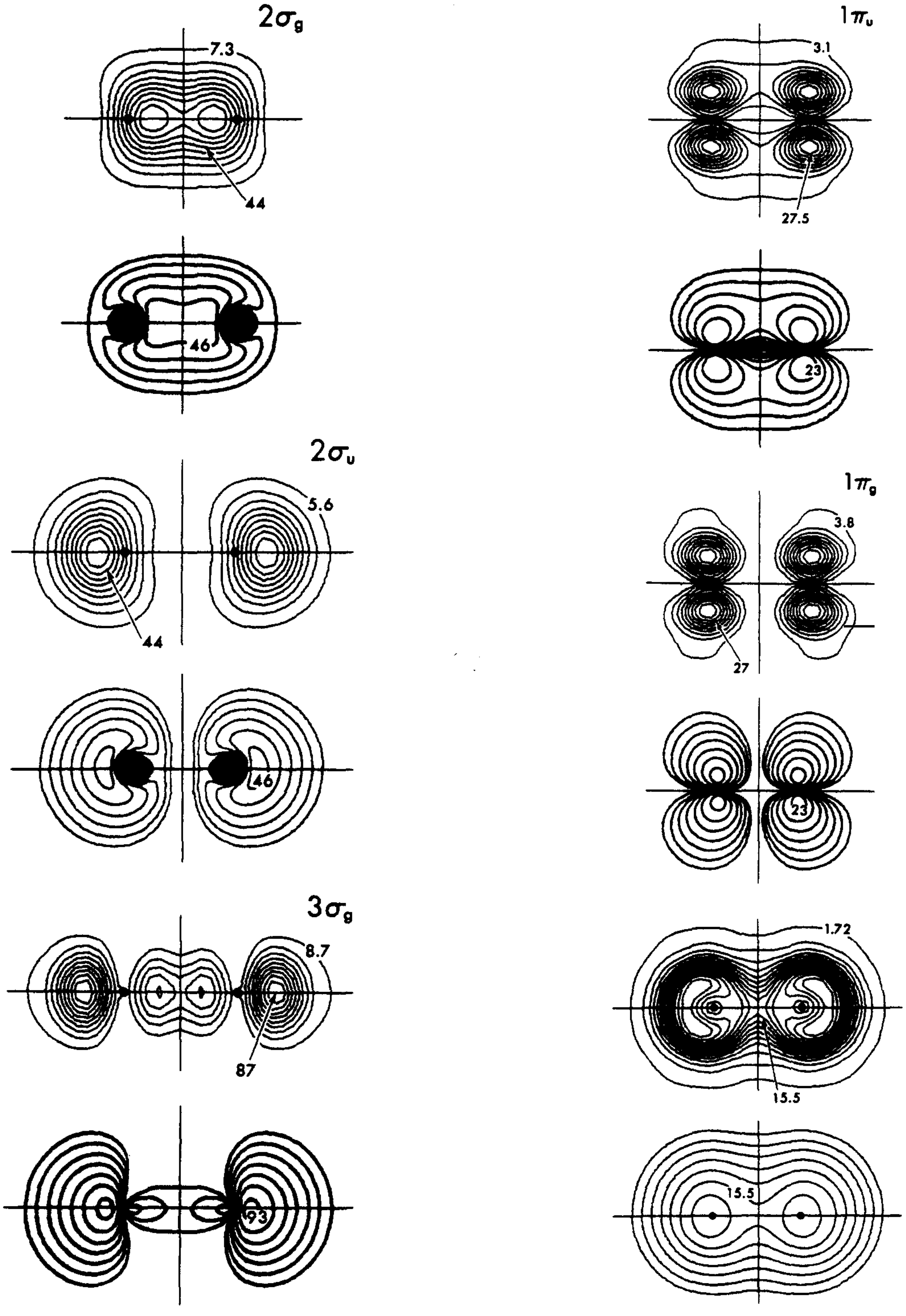

Fig. 2 (a)-(e) $2\sigma_g$, $2\sigma_u$, $3\sigma_g$, $1\pi_u$, $1\pi_g$. The upper contour plots refer to the pseudopotential change densities, the lower plots to the all electron results of Ref. 9. The arrows point to the contours which approximately correspond to each other in space. The contour value associated to one electron in the superlattice unit cell is given for comparison. The smallest contour value of each plot is equal to the contour separation. The black dots indicate the position of the nuclei. (f) Total charge contour plots. Conventions as before.

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