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Theoretical Investigations of the Electronic Properties of Vanadium Oxides. 1. Pseudopotential Periodic Hartree–Fock Study of V_2O_5 Crystal Lattice

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A series of pseudopotential periodic Hartree–Fock calculations has been performed on a V_2O_5 crystal. The optimized V–O bond lengths and stretching force constants are found to be in good agreement with experiment. The band structure and density of states are reported, and in contrast with tight-binding calculations there is no gap in the valence band. From the projected density of state it is shown that the V atom d orbitals play an important role in the bonding and therefore that this oxide is partially ionic. Three types of V–O bonds are recognized in this structure: the mainly covalent vanadyl bond, the ionic bond connecting the central vanadium to the chain oxygen, and the electrostatic–van der Waals bond which ensures the stacking of the layers.

Introduction

Vanadium pentoxide, V_2O_5, presents very interesting properties and is widely used in catalysis,[1] as a n-type semiconductor,[2] and as electrochemical material.[3] Although a large number of experimental studies on this oxide exists,[4] fairly little has been undertaken from a theoretical point of view, especially as concerns the simulation of its transport properties. Computer modeling of such a phenomenon can be achieved using several methods ranging from point defect studies to molecular and lattice dynamics simulations. These methods require the evaluation of the potential energy with respect to the atomic positions which is usually calculated as a sum of two body interactions. In such methods, the pair potential parameters which describe the interatomic forces and the set of effective charges which simulates the electrostatic potential inside the crystal are therefore the key ingredients ensuring the reliability of predicted structural and dynamical properties. Realistic parameters can be extracted either from experimental data such as in "experimental" force field calculations or from electronic-structure calculations performed at a semiempirical or ab initio level.[5] Moreover, it is important to have some ideas about the nature of the bonding because the analytical expressions of the pair potential are different for ionic, covalent, hydrogen, and van der Waals bonds. Ab initio calculations provide a guideline to derive such data as they may give precise informations about the nature of the bonding characteristics and the electronic distribution. Such an approach has been proved successfull in deriving effective pair potentials for molecular mechanics simulations on organic or biological molecules. Application to transition-metal oxide crystals and more generally to solid state inorganic materials is in its earlier stages due to the complexity of the chemical elements involved, especially at the ab initio level of representation.[6] The purpose of the present work is to give more insight into the basic ground-state properties of V_2O_5 at an ab initio HF level so that further empirical simulations could be tackle.

The crystal structure of V_2O_5 has been recently refined[4] and is illustrated on Figure 1. V_2O_5 has an orthorhombic layered structure with only weak van der Waals type interactions between the layers. The position of the atoms in the unit cell are given by Table Ib, whereas the different bond lengths and angles are displayed in Table Ia. Within each layer, one can distinguish V chains in the [010] direction connected by means of oxygen bridges in the [100] direction. The basic unit in the chain is an oxygen pyramid with the vanadium atom in the middle. In the chains these pyramids share edges and are alternatively pointing upward and downward. In the full crystal the building block is a deformed octahedron, whose base is quasiplanar; the shortest V–O bond length corresponds to double (or triple) vanadyl bond (1.577 Å) and the longest one to a weak van der Waals bond (2.791 Å). V_2O_5 consequently presents a structure with an easy cleavage plane, the [001] plane. There are thus three different types of oxygen atoms in the lattice: the chain oxygens, coordinated to two vanadium atoms, in the chains parallel to the vanadium chains; the bridging oxygens, coordinated

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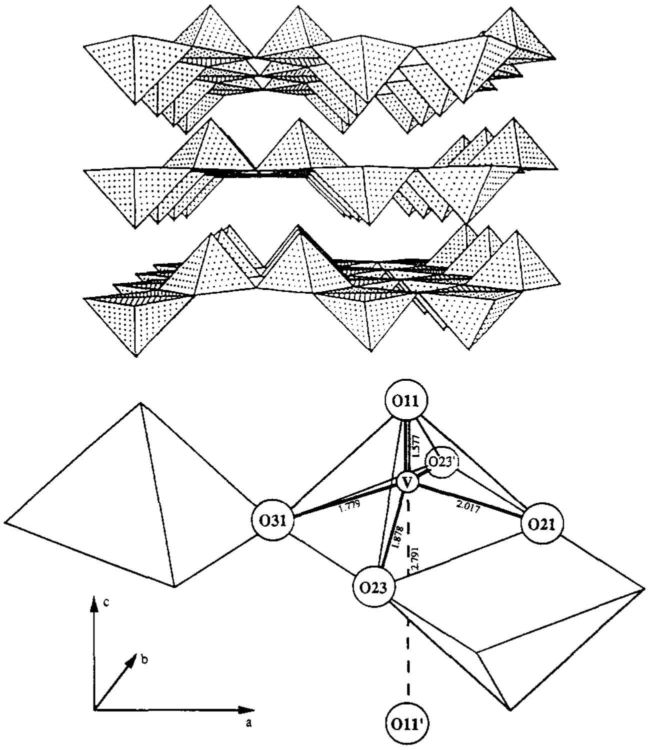

Figure 1. Definition of the coordinate system and atom labeling.

Table I

(a) Experimental[4] Distances (Å) and Angles (°)

V(11)	O(11)	O(31)	O(23)	O(23′)	O(21)	O(11′)
O(11)	1.577(3)	2.652(6)	2.738(4)	2.738(4)	2.868(5)	4.368
O(31)	104.3(2)	1.779(2)	2.742(2)	2.742(2)	3.671(3)	2.857(6)
O(23)	104.5(1)	97.1(1)	1.878(1)	3.564	2.386(4)	2.961(4)
O(23′)	104.5(1)	97.1(1)	143.2(2)	1.878(1)	2.386(4)	2.961(4)
O(21)	105.2(2)	150.5(5)	75.5(1)	75.5(1)	2.017(3)	3.050(5)
O(11′)	177.9(2)	73.7(2)	75.9(1)	75.9(1)	76.9(1)	2.791(3)

	V(12)	V(13)
V(11)	3.427	3.083

(b) Optimized and Experimental[4] Fractional Coordinates and Lattice Parameters

	optimized	experiment
a, Å	11.873	11.512
b, Å	3.630	3.564
c, Å	4.354	4.368
V		
x	0.101 417	0.101 188
y	0.250 000	0.250 000
z	0.881 260	0.891 700
O(11)		
x	0.100 772	0.104 340
y	0.250 000	0.250 000
z	0.531 442	0.531 000
O(21)		
x	0.933 956	0.931 070
y	0.250 000	0.250 000
y	0.011 867	0.003 100
O(31)		
x	0.250 000	0.250 000
y	0.250 000	0.250 000
z	0.976 634	0.001 200

to three vanadium atoms, making a corner between the pyramids in neighbouring chains and the vanadyl oxygen on top of vanadium. Concerning this particular vanadyl bond, experimental evidence exists showing its covalent character.[7,8] Furthermore, IR and Raman vibrational spectroscopic studies[5,7] show that the associated stretching force constant is found of the order of 600 N/m, which is one of the largest values observed among the oxides. Thus a pure ionic description of V_2O_5 is questionable as it has recently been shown that point charge model is inadequate to explain the electric field gradient observed by NMR[8] in V_2O_5 crystals. A detailed calculation of the electronic structure is desirable for future empirical modeling of this material and also to provide a reliable explanation of its properties.

Further interest in the vanadyl oxygen has been stressed by experimental works showing the importance of the vanadyl oxygen vacancy. The presence of defects in the anionic sublattice has a significant influence on the electronic properties of V_2O_5.[9] It is believed to play a role in different processes[10] such as electric conductivity, catalysis and transitions to the related lower vanadium oxides. Oxygen vacancies can initiate a phase transition with rearrangement of the dipole structure and a model involving shifts of the oxygen near the vacancy apparently can be applied to a number of transition metal oxides whose structures are similar to that of V_2O_5.[11]

A number of experimental studies (soft X-ray, EPR, IR spectroscopies) on the electronic structure of V_2O_5 have also been performed,[9] giving several interesting results. But despite this work, many points remain unclear concerning the relationship between the structure of the material and its properties.

To elucidate the electronic factors in determining the behavior of the vanadium pentoxide in both catalytic and insertion phenomena, quantum chemical calculations of the properties of V_2O_5 have been carried out on the bulk material. The electronic structure calculations reported so far belong either to the cluster approach or to periodic calculations carried out with model Hamiltonians in the tight-binding approximation. Ivanovskii et al.[9] simulated the formation of anion defects by V_2O_{12} fragments. Calculations of the electronic structure have been carried out by the LCAO-MO cluster method. This work assumed a constant oxidation state of oxygen of −2 and the charges of V centers were calculated on the using the electroneutrality condition of the oxide $V_2O_{4.09}$. It was shown that the appearance of anion defects in V_2O_5 is accompanied by the narrowing of the oxygen 2s- and 2p-like bands and progressive filling of delocalized metallic d states. Fiermans et al.[12] performed band structure calculations using a tight-binding model of V_2O_5. They notice a greater dispersion along the [010] direction than along perpendicular to the chains. Furthermore, the density of states of the valence band corresponding to the strong vanadyl bond seems in good agreement with XPS results. The authors also try to relate the oxygen vacancy V_2O_3–V_4O_9 and V_2O_5–V_6O_{14}. In the following work of the same team,[13] the authors conclude that a neutral vacancy should formally correspond to V^{3+} rather than V^{4+} but expect that practically only one electron charge is effectively transferred from the vanadyl oxygen to the vanadium in

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Table II. Vanadium and V^{3+} Basis Sets

V					V^{3+}	
d functions		sp functions			d functions	
exponent	coefficient	exponent	s coefficient	p coefficient	exponent	coefficient
28.617 711	0.024 212	19.591 534	0.003 424	0.036 496	29.779 536	0.026 688
7.942 572	0.139 623	4.548 031	−0.193 904	0.193 127	7.896 620	0.160 570
2.535 892	0.361 446	1.188 603	0.563 937	0.483 992	2.522 207	0.403 970
0.889 481	0.479 296				0.919 160	0.474 524
0.288 589	1.000 000	0.300 512	1.000 000	1.000 000	0.333 185	1.000 000

order to minimize intra atomic Coulomb effects and keep the model consistent. In addition, atomic relaxation effects around vacancy were studied semiempiricaly by means of cluster model employing a Born–Mayer potential. The work of Lambrecht[10] is one of the most extensive theoretical studies of V_2O_5. The electronic structure of the ideal, i.e., neutral, unrelaxed vanadyl–oxygen vacancy in V_2O_5 was studied by means of a tight-binding Green function method, based on a single-layer model of the band structure. Optical properties and analysis of the splitting of the two-electron neutral vacancy ground state was performed in relation to the EPR spectra of V_2O_5. The picture of the oxygen vacancy emerging from this study is characterized by fairly deep, electrically inactive traplike levels, strongly localized on the central vanadium.

While giving valuable information, these approaches suffer from several approximations. On one hand, in tight-binding theories only nearest-neighbor repulsion is taken into account, and therefore the importance of the attractive potential due to distant atoms is overestimated. On the other hand, clusters of nearest neighbors of an atom in the crystal lattice are only concerned with localized electron states neglecting the long-range effects. The ideal method is thus to consider all the possible interaction in the whole crystal lattice. We present here such investigations at the SCF level using core pseudopotentials with infinite periodic structures. The paper also illustrates the value of periodic Hartree–Fock calculations and how they can provide accurate structural and electronic descriptions of this pronounced ionic–covalent structure. In addition to providing information on the electronic structure of V_2O_5, these ab initio calculations are also used in a separate study to derive good quality empirical potential functions,[14] which may then be used to model structures and defect properties on the material.

Method of Calculation

The calculations have been performed with an improved version of the periodic Hartree–Fock program CRYSTAL[15] developed by Dovesi and co-workers. This program solves the Hartree–Fock–Roothaan equations for periodic systems. The crystalline orbitals are expanded in terms of Bloch functions themselves expressed on a localized atomic orbital basis set. A detailed description of the method can be found in the book of Pisani et al.[16] The program works at the all electron (AE) level as well as with effective core pseudopotentials (ECP). In this approach only the valence electrons are explicitly taken into account, and the calculated total energy corresponds to the sum of the ionization potentials of the valence orbitals. It has been shown[17] that the Durand and Barthelat ECPs[18] yield results as accurate as AE ones computed with similar quality basis sets.

A satisfactory AE description of the vanadium core shells would involve a rather large number of basis functions and therefore noticeably increase the computational effort with respect to an ECP calculation. Moreover the ECP approach is expected to minimize the basis set superposition error (BSSE) since the variational flexibility of the basis set is, in this case, only used to describe the valence regions. The oxygen basis, the PS-31G set,[19] yields a total energy $E_T = -15.631\,872$ hartrees, which differs from the sum of the six first ionization potentials[20] by 0.279 hartree, corresponding to the estimate of the correlation energy (0.258 hartree).[21] For vanadium, a (5d/3s) contracted to a [41/21] basis set has been optimized by the method outlined in ref 19. The starting point of the exponent optimization is the valence and d functions of the (3333/33/5) set of Huzinaga.[22] The exponent and contraction coefficients are reported in Table II.

For the isolated V atom in its ground state the total energy calculated with this basis set is $E_T = -6.025\,675$ hartrees. The 3d and 4s pseudoorbital eigenvalues closely match the AE values one can obtain with the Huzinaga's set.[22] The pseudopotential total energy differs by only 0.009 hartree from the sum of the first five experimental ionization potentials.[20] This difference is not significant because two of the experimental ionization potentials are given only to the nearest electronvolt. In actual crystalline calculations on V_2O_5 the standard 4s AOs do not contribute to the ground-state wave function since V_2O_5 is largely ionic. Moreover, such diffuse orbitals might be responsible for basis set linear dependence. A single exponent 4sp shell has been first added to the standard 3d set for polarization purposes. The Mulliken population analysis of the crystalline calculation carried out with this basis set indicates that the vanadium centers are almost V^{3+} and that this sp shell does not contribute to the ground-state wavefunction. Therefore, in order to minimize the cost of the calculation, this shell has been removed and a [41] contraction of 5 d atomic orbitals optimized on the V^{3+} cation, also listed in Table II, used instead of the neutral atom basis set. With this basis set the calculation

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of a single energy value requires about half an hour of CPU on a VP200 computer.

Results and Discussion

Structure Optimization. As mentioned in the Introduction, vanadium pentoxide crystallizes in the *Pmmn* space group and its structure is defined by the three lattice parameters *a*, *b*, *c* and seven fractional coordinates, two of which are close to zero. A full geometry optimization implies that 10 parameters have to be varied. This would be tractable with a program including analytical evaluation of energy gradient, but this facility is not available in CRYSTAL.

The crystallographical coordinate system is not the most convenient to carry out structure optimization. Internal coordinates, which are close to normal coordinates yield, in general, nearly diagonal force fields allowing us to discriminate between stiff and soft coordinates and thus to set up a strategy for the optimization process. The internal coordinates used herein are defined in Figure 1. The transformation from internal to crystallographical coordinates can be greatly simplified by assuming that the four oxygen which constitute a face of the V_2O_5 pyramid are in the basal plane. This approximation induces errors in the lattice parameters which are les than 0.5%.

Two experimental force fields have been reported so far in the literature. On one hand is the valence force field of Abello et al.[5] and on the other hand is the Urey–Bradley force field of Clauws et al.[7] In both force fields the interaction constants between stretching coordinates are rather large compared to the corresponding diagonal constants. This is not the case either for the vanadyl bond or for the long V–O (2.79 Å) which ensures the stacking of successive layers. Therefore these two coordinates can been optimized independently. The optimization of the other structural parameters is difficult because of the strong coupling between the other V–O bonds.

The optimized vanadyl bond length (R_1), 1.528 Å, is shorter by 0.03 Å than the experimental one.[4] The calculated force constant, 663 N/m, is in good agreement with both experimental values.[5,7] Since Hartree–Fock calculations do not account for the dispersion forces which are in part responsible for the cohesion of the layers, the second optimized V–O bond length (R_3) is found to be longer than the experimental one by 0.15 Å. The associated force constant is calculated of the order of 10 N/m, the third of the experimental value.

The optimized values of the V–O (31), V–O (21), and V–O (23) bond lengths are respectively 1.824, 2.074, and 1.940 Å. They are larger than the experimental ones by about 3%. We have not calculated the stretching force constants associated with these internal coordinates because of their strong coupling. Finally the optimized ∠O(11)–V–O(21) is found to be very close to experiment: 105.5 against 105.2°. Overall, the agreement between measured and calculated structure parameters is satisfactory.

Binding Energy. The total energy per cell with the experimental structure is −180.628 357 hartrees, which corresponds to a binding energy of −0.1835 hartree. The "experimental" binding energy can be roughly estimated from the standard heat of formation of vanadium oxide[23] and from the heat of atomisation,[20] neglecting the zero point motion and specific heat contribution one finds −2.93 hartrees. The difference (1.7715 hartrees) between the experimental and Hartree–Fock binding energies is due, in part, to correlation effects which can be evaluated by a post SCF correction involving a density functional approach. The Perdew[24] and Colle and Salvetti[25] functionals yield about 0.5 hartree of extra binding energy. About the same amount is expected to be gained from geometry optimization and the remaining error should be traced to basis set limitations, due in particular to the lack of polarization functions.

Table III. Mulliken Population Analysis

Net Charge	
V	+2.280
O(11)	−0.493
O(21)	−1.271
O(31)	−1.032
Bond Population	
V–O(11)	0.359
V–O(11′)	0.003
V–O(21)	0.162
V–O(23)	0.097
V–O(31)	0.062
Orbital Population	
V $3d_{3z^2-r^2}$	0.870
V $3d_{xz}$	0.517
V $3d_{yz}$	0.513
V $3d_{x^2-y^2}$	0.568
V $3d_{xy}$	0.248
O(11) 2s	1.948
O(11) $2p_x$	1.624
O(11) $2p_y$	1.608
O(11) $2p_z$	1.313
O(21) 2s	1.945
O(21) $2p_x$	1.789
O(21) $2p_y$	1.679
O(21) $2p_z$	1.861
O(31) 2s	1.932
O(31) $2p_x$	1.552
O(31) $2p_y$	1.740
O(31) $2p_z$	1.812

The stacking of the layers is due to electrostatic and dispersion forces. In principle only the electrostatic interaction energy is accounted for at the Hartree–Fock level whereas the correlation corrections are expected to bring a part of the dispersion interaction. Comparison between bulk and slab calculations shows that the electrostatic (0.0236 hartree/cell) and dispersion (0.0294 hartree/cell) contributions are calculated to be very weak and of similar magnitude. This explains the low value of the stretching force constant associated to the longer V–O bond reported by Abello et al.[5]

Bonding Properties. *Population Analysis and Electron Density.* The Mulliken population data reported in Table III show that the vanadium oxide is a partially ionic system. The oxygen net charges range from −0.493 for the vanadyl oxygen to −1.271 for those involved in the bonds directed along the *a* axis. The covalent character of the vanadyl bond is reflected by the rather large bond population of the vanadium $3d_{3z^2-r^2}$ orbital. Though it is not possible to derive oxygen ionicities on an absolute

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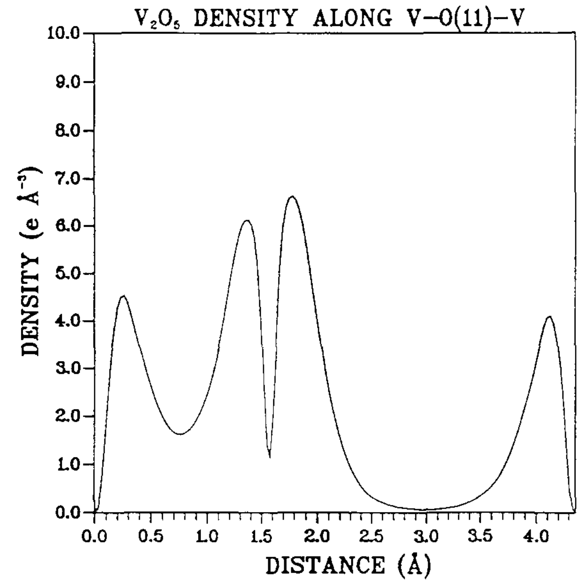

Figure 2. Electron density along the O(11) V and V O(11′) directions.

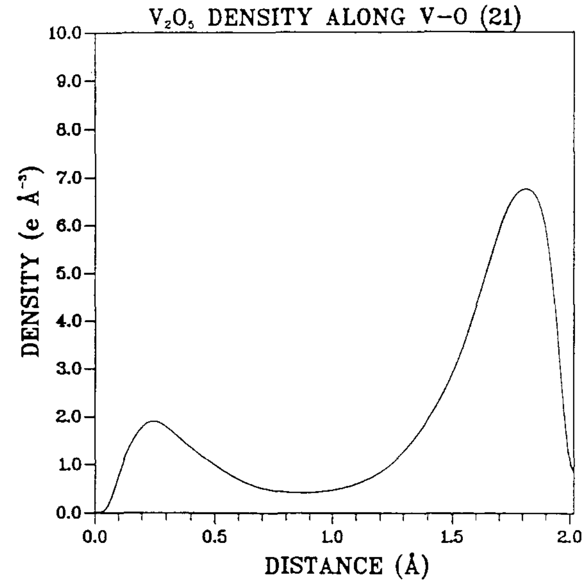

Figure 3. Total valence electron density along the V O(21) direction.

scale from the Mulliken population analysis, this technique provides a reliable classification.

Figures 2–5 display the total valence electron density along the different vanadium oxygen bonds. The left and right parts of Figure 2 correspond to the vanadyl and to the long V–O bonds respectively. The vanadium wing density maximum on the vanadyl side is rather high (4.5 e$^-$ Å^{-3}) and a noticeable density (1.8 e$^-$ Å^{-3}) remains at the middle of the vanadyl bond. On the other side, note first a slight increase of the oxygen density and the large low density interlayer region. The density along the V–O (21), V–O (31), and V–O (23) bonds are characterized by a low density maximum on the vanadium side (about 2.0 e$^-$ Å^{-3}) and at the middle of the bonds. The density appears to be almost the superposition of the contributions of the cation and anions. The maximum densities on the oxygen side are in an order that is consistent with the population analysis data. In fact these three bonds are found ionic whereas the vanadyl bond is mostly covalent and the interlayer bonds due to electrostatic and van der Waals interactions.

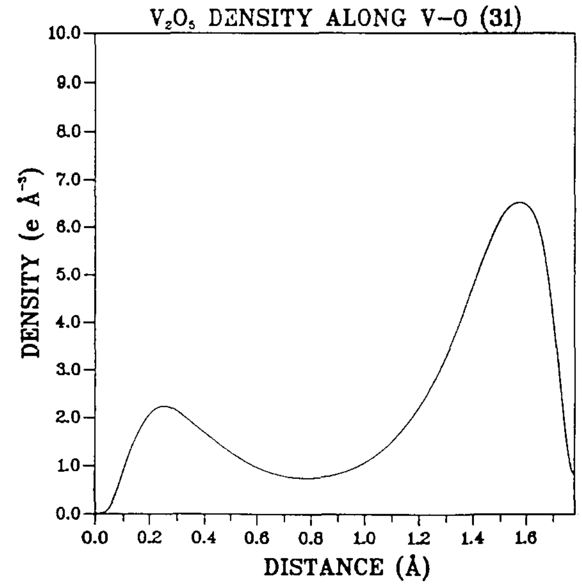

Figure 4. Total valence electron density along the V O(31) direction.

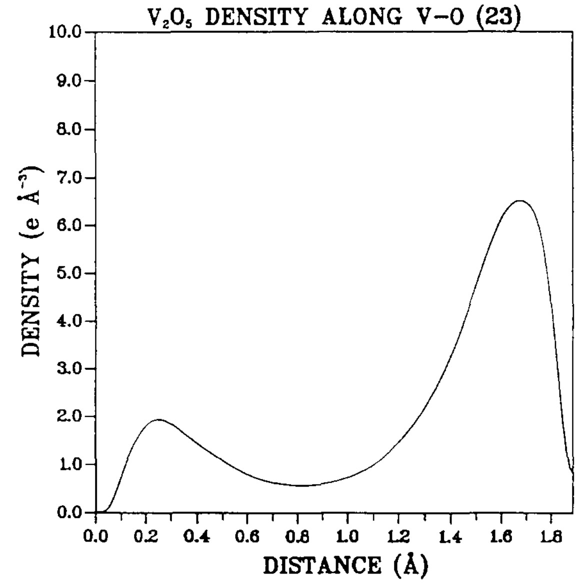

Figure 5. Total valence electron density along the V O(23) direction.

Figure 6 displays the total valence density map in the [040] plane. The density around the bridging oxygens (23) is almost spherical with bulges towards the vanadium centres; the minima along the corresponding bonds correspond to a low density between 1.0 and 0.5 e$^-$ Å^{-3}. Note the low density regions between and below the vanadyl oxygens.

Band Structure and Density of States. The band structure along the high-symmetry lines of the Brillouin zone is presented in Figures 7.[29] The topology of this band structure is slightly different from these previously computed with a parametrized Hamiltonian by Lambrecht et al.[10] and by Bullett.[26] In contrast with our results these authors find a forbidden gap of width of about 2.8 eV separating the V–3d and O–2p states of the valence band. A very similar band structure (not presented here) is produced with the basis set involving a sp shell on V centers, and therefore the discrepancy between the periodic

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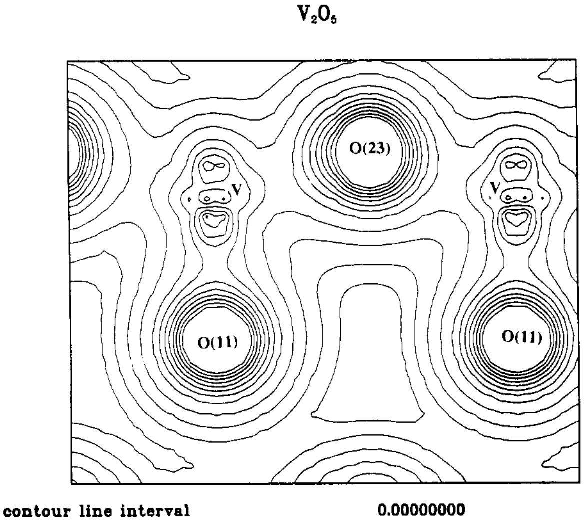

Figure 6. Total valence electron density in the [040] plane. The contours are at 0.0625, 0.125, 0.25, 0.5, 1.0, 1.5, etc., e Å^{-3}. The bold lines correspond to 3.5 e Å^{-3}.

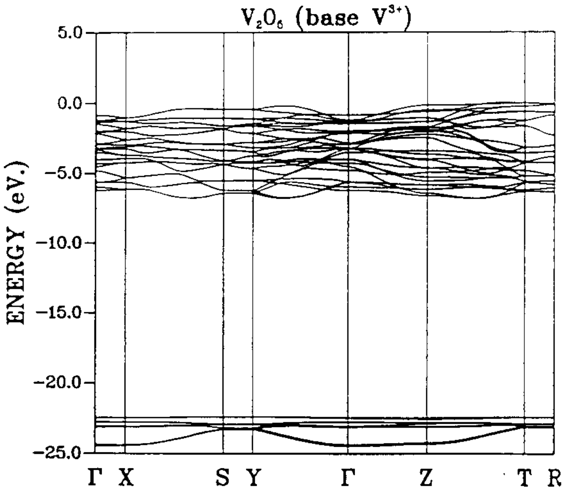

Figure 7. Band structure of vanadium pentoxide. The origin of the energy scale is taken at the Fermi level. The notation which identifies Brillouin lines is the standard one; see ref 29. The numbers of bands in the upper and lower band complexes is obtained according to the nonsymmorphic space group at the V_2O_5 structure which contains two formula units per cell.

Hartree–Fock band structure and the tight-binding one is not due to an artefact of basis set. In the Hartree–Fock framework the vanadium d orbitals are allowed to form covalent bonds. In Figure 7 the topmost occupied states correspond to the oxygen lone pairs and to the vanadyl bond whereas the lowest states are essentially due to the 2s oxygen orbitals. In agreement with the previously mentioned calculations there is a large gap of about 20 eV. between these two groups.

The band gap at Γ is of the order of 12 eV, and therefore vanadium pentoxide is calculated to be insulator. The magnitude of the gap is greatly in excess of the experimental value of ~2.3 eV;[27] but such exaggerations of the gap are normal in Hartree–Fock calculations in which the unique requirement for unoccupied states is that they must be orthogonal to the occupied ones.

The projected density of states plotted on Figures 8 and 9 confirm the assignment of the band structure made above. In addition it shows that the vanadium 3d orbitals, which are a noticeable constituents of the valence band, do contribute to the bonding since a rather large contribution is found mixed to the bonding 2p oxygen states between −4.0 and −6.5 eV.

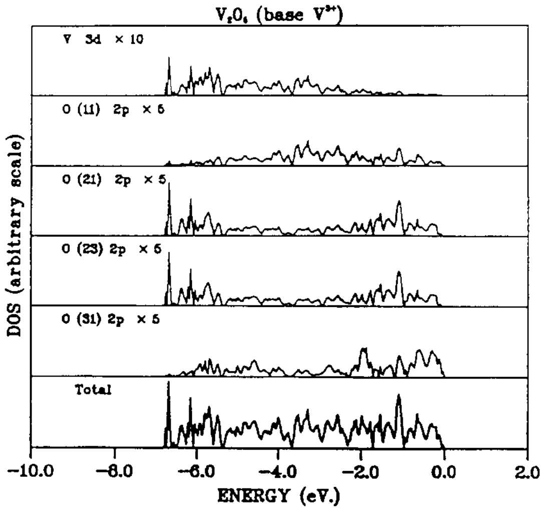

Figure 8. Total and projected density of states; the origin of the energy scale is taken at the Fermi level.

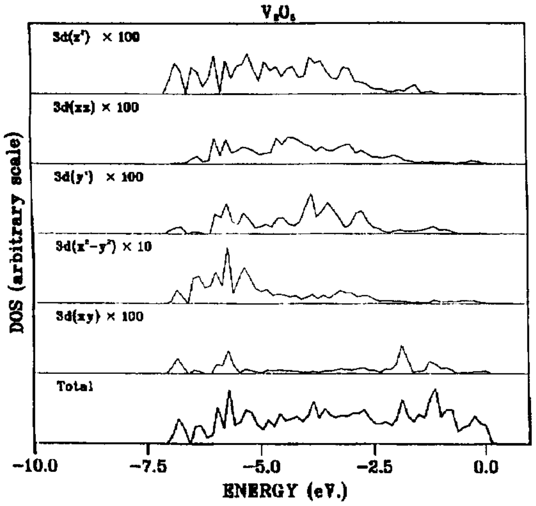

Figure 9. Total and projected density of states for 3d vanadium orbitals; the origin of the energy scale is taken at the Fermi level.

Conclusion

In spite of basis set deficiency, the Born–Oppenheimer energy surface appears to be reliable. An interesting result is the evidence from the projected density of states analysis of the contribution of the vanadium 3d orbitals to the bonding. This corresponds to a picture in which the V^{3+} cation has lost its two 4s and a 3d electrons and forms a covalent bond with the vanadyl oxygen. This bond is intermediate between a single and a double bond. The four remaining V–O bonds are essentially ionic, as indicated by the valence electron density plots. The weakness of this calculation is the very low binding energy calculated, even after correlation. Its strength is the good agreement obtained for the structural parameters and for the vanadyl bond stretching force constant.

The results presented here show that the periodic Hartree–Fock method provides a convenient scheme to perform numerical studies on *transition-metal* oxides. Moreover the reliability of the effective core pseudopotential approach is an evidence by this study. On one hand the calculation fairly reproduces the vanadyl bond length and related force constant, and on the other hand it provides useful informations on the bonding properties. In particular the role of the vanadium 3d orbital is emphasized. We hope that it will be possible in the near future to carry out calculations with an improved basis set and also to take electron correlation into account.

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