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## LETTER TO THE EDITOR

# A calculation of the cohesive properties of solid methane by a local orbital approach, including correlation

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**Abstract.** The use of the *ab initio* Hartree–Fock local orbitals method in solid state computations has been limited primarily to the cases of simple solids such as alkali halides, solid rare gases and the ceramics. This usage has been mostly limited to the study of energy band structures and to the case of impurities and point defects in these systems. The only exceptions to these statements are energy band calculations for solid methane and calcium, and a study of the edge dislocation in RDX. In this report, techniques to extend the utility of the local orbital methods for the determination of geometry are explored, with a particular emphasis on the study of molecular solids. The method may be extended to include elevated pressures and also allows the study of point or extended defects and impurities simultaneously. It is also possible, using previously defined methods, to obtain the energy band structures for such systems. In this initial report a study of the equilibrium lattice properties of solid methane is made.

Theoretical studies of three-dimensional solids frequently exclude the class of molecular solids, the principal exception to this statement being the rare gas solids. In addition some attention has been paid to solid H<sub>2</sub>, largely due to interest in its possible metallization. More complicated molecular solids, those which have more than one atom type in a molecule, or perhaps more than one molecular type in a unit cell, are frequently studied in one-dimensional situations (polymers), rather than in three-dimensional situations. The most notable exception to this is the case of solid methane (CH<sub>4</sub>), for which a number of solid state energy band calculations exist (Piela *et al* 1973, Kunz 1983a). In many respects, these calculations have been rather successful in that they account for the dominant features of the optical spectrum of solid CH<sub>4</sub> and also for the observed features in the density of states.

The existing calculations form an incomplete study of solid CH<sub>4</sub> in that the equilibrium lattice properties, such as the solid density, cohesive energy and solid C–H distance are not computed at all, and those equilibrium lattice properties needed for input to a band structure calculation (lattice type, lattice parameters) are taken from experiment. In this respect, solid CH<sub>4</sub> might serve as a prototype for computational methodology on more complex molecular solids. The particular features that may complicate the study include the strong and relatively stiff C–H bond within the CH<sub>4</sub> molecule and the relatively weak bond between pairs of molecules. In this instance, the dominant bonding between CH<sub>4</sub> pairs is the Van der Waals force. Thus any useful computation will have to accommodate bonding strengths at two distinctly different levels of strength, both of which ultimately determine the density and bonding strength of the solid CH<sub>4</sub>.

The method chosen here is a derivative of the Hartree–Fock local orbital method used for studies of alkali halide, solid rare gas and CH<sub>4</sub> band structures (Kunz 1969, 1983b, Kunz

and Mickish 1973). This method has been modified in several significant ways however. These modifications include provision for computing the cohesive energy of the solid, with and without inclusion of Van der Waals forces as a function of solid and molecular geometry. These calculations are accomplished within the local orbital method and do not require the calculation of any band structure information as such. Thus these calculations are strictly  $N$ -body ground state calculations.

The basis of this calculation is the  $N$ -electron Hamiltonian for the system:

$$H\Psi_0 = E_0\Psi_0$$

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^n \nabla^2 - \sum_{i=1}^n \sum_{I=1}^N \frac{e^2 Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_i^n \sum_j^n \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + V_{NN}.$$

Here, lower case is used to reference electron properties:  $m$  for mass,  $e$  for charge,  $\mathbf{r}$  for position. Upper case letters refer to nuclear properties,  $Z$  for atomic number and  $\mathbf{R}$  for position. There are  $n$  electrons in the system and  $N$  nuclei. If one assumes that the wavefunction,  $\Psi_0$ , may be replaced by a single Slater determinant, the usual Hartree-Fock approximation results. That is

$$F(\rho)\phi_i = \varepsilon_i\phi_i$$

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i \leq n} \phi_i(\mathbf{r}_1)\phi_i(\mathbf{r}_2)$$

$$F(\rho) = -\frac{\hbar^2}{2m} - \sum_{I=1}^N \frac{e^2 Z_I}{|\mathbf{r}_1 - \mathbf{R}_I|} + e^2 \int \rho(\mathbf{r}_2, \mathbf{r}_2)/|\mathbf{r}_2 - \mathbf{r}_1| d\nu_2$$

$$- e^2 \rho(\mathbf{r}_1, \mathbf{r}_2)/|\mathbf{r}_1 - \mathbf{r}_2| P(\mathbf{r}_2, \mathbf{r}_1).$$

$F$  is termed the Fock operator,  $\rho$  is the first-order density matrix;  $P$  is the permutation operator that replaces coordinates in space 1 with those in space 2. When solved canonically, this results in a Hartree-Fock determination of the band structure and may also provide a total energy. A current method for this is the CRYSTAL92 code (Dovesi *et al* 1992). The current methods for solving the canonical Hartree-Fock problem do not allow for a direct inclusion of Van der Waals type forces and therefore are not fully useful for either total energy computations for solid  $\text{CH}_4$  or for calculation of other properties in which electron correlation plays a significant role.

It is possible to circumvent this problem for non-metals by employing the method or local orbitals (Adams 1962, Gilbert 1963, Kunz 1983b). Here one performs a canonical transformation on the Hartree-Fock problem. This is obtained by using a localization operator,  $W$ , which interrupts periodicity and therefore allows solutions that decay with distance, rather than having Bloch periodicity. This is done in solving the following set of equations:

$$[F_A + U_A + \rho W \rho] \hat{\phi}_i = \hat{\varepsilon}_i \cdot \hat{\phi}_i$$

$$U_A = V_A^S + V_A^{PI}$$

$$[F_A + V_A^{PI} + V_A^S - \rho V_A^S \rho] \hat{\phi}_{Ai} = \hat{\varepsilon}_{Ai} \hat{\phi}_{Ai}$$

$$\rho_A(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i \in A} \hat{\phi}_{Ai}(\mathbf{r}_1) \hat{\phi}_{Ai}^*(\mathbf{r}_2).$$

**Table 1.** The exponents and the coefficients of the Gaussian basis functions used in this CH<sub>4</sub> calculation. The basis functions employ Cartesian Gaussian form as indicated. The radial part of the basis function is defined as  $R_j(r) = \sum_j c_j^i e^{-\alpha_j r^2}$ .

Orbital	Angular type	Centre	Exponent	coefficient
1	s	C	5234.2999	0.0009455
			770.02922	0.0074134
			175.70596	0.0367802
			50.530790	0.1308681
			16.739168	0.3214182
2	s	C	6.0883290	0.4472833
			2.3133133	0.2082753
3	s	C	5.1580033	-0.0848225
			0.47453327	0.5728404
4	s	C	0.14915291	1.0
5	s	C	0.7	1.0
6	p	C	53.537810	0.0026615
			12.278300	0.0193971
			3.7448981	0.0808426
			1.3306550	0.2247661
			0.50924661	0.3889074
7	p	C	0.19832945	0.3875806
			0.07700000	0.1386347
			0.8	1.0
8	p	C	0.8	1.0
9	d	C	0.9	1.0
10	s	H	102.5	0.001005
			16.00	0.016821
			1.700	0.183761
			0.330	0.610353
11	s	H	0.085	1.0
12	p	H	0.5	1.0

In this set of equations one picks  $W$  to be  $-V_A^S$ . Here the system has been partitioned into a local fragment designated  $A$ , and an environment of  $A$ . In periodic systems, the environment of  $A$  may be composed of fragments identical to  $A$ , but displaced to other lattice positions. In the usual CH<sub>4</sub> band structure, one chooses  $A$  to be a CH<sub>4</sub> molecule, but since a direct determination of Van der Waals forces between pairs of CH<sub>4</sub> molecules is needed, the best choice of the crystal fragment  $A$  is the choice of nearest-neighbour CH<sub>4</sub> molecule pairs. This facilitates a direct computation of the correlation energy (Van der Waals attraction) of the solid, by obtaining the pair molecular correlation energy self-consistently in the field of the remainder of the solid. Computation of the correlation energy may be done by direct use of many-body perturbation theory (MBPT) on the fragment and summing such a result over the entire solid. This was introduced for exciton calculations in alkali halides by Goalwin and Kunz (1986) and extended by Kunz and co-workers (1988). The second-order contribution to the total energy of fragment  $A$  is given as

$$E_0^{(2)} = \sum_{I \neq 0} \frac{\langle \Psi_0 | H | \Psi_I \rangle \langle \Psi_I | H | \Psi_0 \rangle}{E_0^{(0)} - E_I^{(0)}}$$

$$E_j^{(0)} = \sum_{i=\text{OCC}} \hat{\epsilon}_{Ai}$$

This then is the system of equations to be solved for the fragment consisting of two CH<sub>4</sub> molecules in the periodic environment of other CH<sub>4</sub> pairs.

The only remaining approximations consist of fixing the H atoms in a regular array, tetrahedrally coordinated to each C, and also periodic, and the use of basis set expansion techniques to solve the equations. This ignores the fact that while each C has four H tetrahedrally coordinated to it, the H in solid  $\text{CH}_4$  are rotationally disordered. This is a reasonable approximation in that the rotational disorder implies that the rotational state of a given  $\text{CH}_4$  molecule is of small consequence to the total energy. The basis sets used are chosen by minimizing the energy of the individual  $\text{CH}_4$  molecule in free space, to second order in MBPT. The basis set is a relatively rich one, and is shown in table 1.

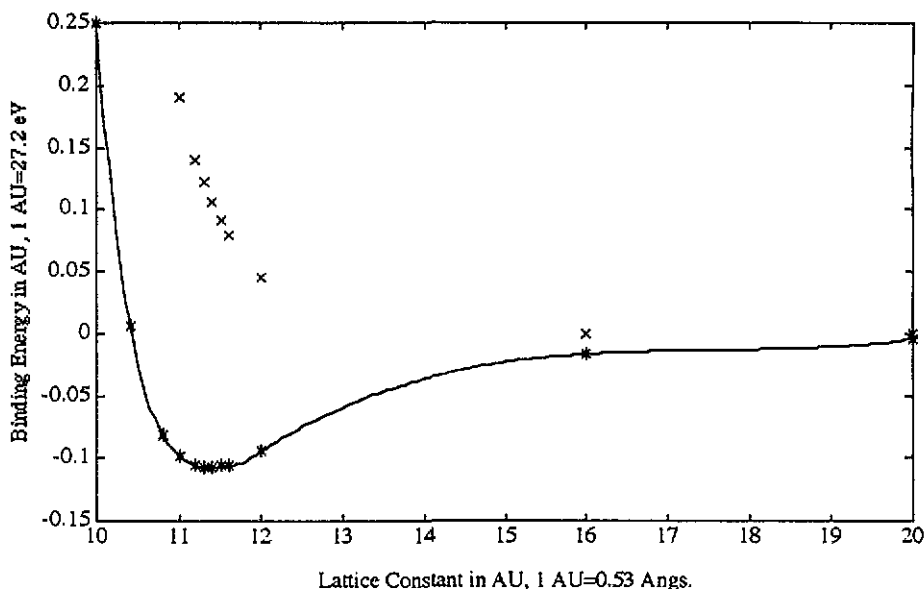


Figure 1. The binding energy of solid  $\text{CH}_4$  is given as a function of the lattice constant. Distances are in atomic units, and energies are in electronvolts. The zero of energy refers to an ensemble of  $\text{CH}_4$  molecules infinitely separated from each other. The correlated computation has its points designated by the symbol \*, whereas the Hartree-Fock computation has its points labelled by an x. The curve for the correlated calculation has been obtained from a cubic spline fit to the computed points.

The lattice used in these studies is the FCC lattice, which is the lattice occupied by the C atoms in solid  $\text{CH}_4$  as determined experimentally (Shallamach 1939, Press 1972, Wannier 1959). Within this lattice, the C-C distances and also the C-H distances are allowed to vary. It was rapidly determined that the C-H separation for minimum total energy of the solid was essentially identical to that found in the free molecule, and that small decreases in the C-H separation occurred only for significant compression of the solid. Therefore in the results to follow the C-H separation in the free  $\text{CH}_4$  is used. The crystal binding energy is shown in both the Hartree-Fock approximation and including Van der Waals terms in figure 1. The zero of binding energy refers to the energy per molecule when the  $\text{CH}_4$  molecules are at infinite separation. The lattice constant is computed to be 11.35 au (the experimental value is 11.30 au) for an error of 0.5%. The binding energy is found to be 0.107 eV/molecule (the experimental value is 0.117 eV) for an error of about 10%. The binding is entirely due to Van der Waals forces as may be readily seen from the figure. It

is also worth noting that the use of the extensive basis set was needed in order to obtain the relatively accurate binding energy and the lattice constant.

In conclusion, an extension to the local orbital method, including both Hartree-Fock terms and Van der Waals terms, has been developed and used here to predict the lattice parameter and the binding energy of solid  $\text{CH}_4$ . Accurate results were possible, and care was required in the choice of the basis set to enable an accurate determination of the Van der Waals energy. The method allows determination of geometries within the fragments chosen to represent the crystal as well as the geometries of the fragments with respect to each other. This capability is of minimal use here as individual  $\text{CH}_4$  molecules maintain the geometry of the free  $\text{CH}_4$  inside the solid, but may well be significant in studies of more complex molecular solids. Such studies are in progress.

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