Semiempirical LCAO calculations of electronic and dynamical properties of α and γ nitrogen crystals and nitrogen aggregates

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Semi-empirical LCAO methods (extended Huckel, iterative extended Huckel and INDO) are examined as a possible simple starting point for constructing solid state interaction potentials for non-bonded interactions from molecular wave functions. These methods are applied to calculate the cohesion energy and lattice equilibrium unit cell dimensions for α and γ nitrogen crystals, the lattice optical mode frequencies at $\tilde{q}=0$ of $\alpha-N_2$, the electronic Davydov splitting of the molecular $^1\Pi_g$ state in $\alpha-N_2$ and the stability of molecular-ion aggregates. Reasonable agreement is obtained with extended Huckel and iterative extended Huckel methods, while INDO usually yields poor results. The possibility of excimer formation in nitrogen is discussed in light of these calculations. It is concluded that semiquantitative results can be obtained with these methods when they include the gross features essential for description of crystal non-bonded interactions, such as full overlap interactions, approximate magnitude of molecular permanent quadrupole moment, orthogonality corrections and self-consistent charge transfer. However, when more accurate results are required, *ab initio* methods cannot be avoided.

1. Introduction

The intermolecular potential energy determining electronic properties of molecular crystals and aggregates is usually treated either as an empirical function of adjustable parameters selected to yield some of the experimental properties of the fluid and crystal [1–4], or by *ab initio* evaluation from the electronic wave function of the isolated molecule [5, 6]. While the first approach is usually completely inductive in nature and thus depends on the availability of sufficient experimental data, the latter approach is laborious and can be applied only to a limited number of relatively simple problems. It is the purpose of this paper to examine the possible usefulness of an intermediate approach. The approach is based on the representation of intermolecular non-bonded interactions in the solid by an interaction potential that is calculated from the solution of the LCAO problem of a cluster of two or more molecules. The wave functions are determined by semi-empirical molecular orbital methods, parameterizing only free atom properties, such as the extended Hückel (EXH) [7], iterative extended Hückel (IEXH) [8] and INDO [9] methods. These LCAO methods have been successfully used for studying both bonded interactions in atomic solids [10–13] and non-bonded intermolecular interactions in molecular dimers such as excimer stability [14, 15], molecule-ion interactions [16] and intermolecular reaction

paths [17–19].   It was suggested that the application of the all-valence electron M.O. approach retaining all overlap integrals to dimers, by considering them as a ' supermolecule ', could reveal the gross feature of the ground and excited state interaction potential of a dimer [20].   In this paper we extend the use of these methods to describe both dynamical and electronic properties of a solid molecular system, thus examining the possible applicability of the MO–LCAO potential to molecular crystals.   We chose to construct these potentials for the α and γ forms of crystalline nitrogen, nitrogen dimers and molecular-ion dimers because of the availability of extensive experimental and theoretical work on the ground state anisotropic potential [3], crystal structure [21, 22] cohesive energy [23], lattice libration [24–26] and translation mode frequencies [27, 28], electronic Davydov splitting and spectral shift [29–30] and ion-molecule interactions [31–32].

2. Choice of molecular wave functions

The quantum chemical methods EXH, IEXH and INDO were used to obtain the cluster wave functions.   The EXH method contains one free para-meter, namely the proportionality constant between off-diagonal electronic matrix elements and the overlap multiplied by the sum of diagonal matrix elements.   For organic molecules, the value of this parameter was adjusted to be 1·75 [7] so that it correctly simulates the barrier for internal rotation in ethane, while for inorganic problems this parameter is usually set between 1·50 and 1·70. We treated this as an adjustable parameter to obtain the best agreement with the bond length, ionization potential† and dissociation energy of the N_2 molecule. Using Slater $1s$, $2s$, $2p_x$, $2p_y$ and $2p_z$ atomic orbitals for each atom, with the $2s$ state orthogonalized to the inner $1s$ orbital by Schmidt's process, and taking atomic orbital energies from Hartree–Fock calculations on the ^4S atomic ground state [34], the value of this parameter was found to be 1·66.

IEXH method contains no free parameter, and the Hamiltonian matrix elements are taken to depend explicitly on the net atomic charges to account self-consistently for charge redistribution when the molecules are brought together to form a cluster.   A charge self-consistent intermolecular interaction potential can thus be calculated by this method.   Atomic charges are calculated from one- and two-centre contributions to the charge moment by a procedure that leaves the projection of the centroid of charge on the line connecting the atoms unchanged. The free atom orbital energies were again taken from atomic Hartree–Fock calcu-lations, and the charge dependent part of the atomic potential from the original work of Rien et al. [8].

Although the INDO method neglects most of the interactions on which the intermolecular energy depends, it has been used previously extensively in calculat-ing the ground state intermolecular potential for describing reaction mechanisms in various systems [18, 19].   Hence, we have examined to some extent the crystal properties calculated by the INDO potential.   As expected, this method fails completely in revealing a reasonable non-bonded intermolecular potential for calculation of solid state properties in the examined system, and was therefore rejected in further calculations.   The INDO calculations were performed with the usual atomic parametrization of Pople and Segal [9].

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† Ionization potentials were calculated according to Koopman's theorem.   Recently [33] this theorem was shown to fail to predict accurate differential vertical ionization potentials.

In table 1, the results for a single N_2 molecule, calculated by the discussed semi-empirical methods are summarized and compared with the minimal basis set Hartree–Fock calculations of Ransil [35], the more refined Hartree–Fock calculations of Cade [36], and experimental thermochemical and photoelectron [37] results.

| Property | EXH | IEXH | INDO | Hartree–Fock | | Experiment |
				Minimal set (a)	Large set (b)	
Dissociation energy/ eV	7·32	9·76	20·21			9·760 (d)
Ionization potential/ eV	15·12	16·1	16·32	14·82	17·10	15·60 (e)
$E_{2\sigma u}$/eV	20·92	20·70	22·84	19·88	20·92	18·78 (e)
$E_{\pi u}$/eV	17·38	17·82	20·13	15·77	17·10	16·98 (e)
$E_{2\sigma g}$/eV	15·12	16·10	16·32	14·82	17·36	15·60 (e)
Equilibrium $^1\Sigma_g$ distance/Å	1·17	1·15				1·098 (c)
Equilibrium $^1\Pi_g$ distance/Å	1·20	1·21				1·213 (c)
Vibrational wave-number/(cm⁻¹)	1,650	1,800	11,300			2,373 (c)

eV $\approx 0\cdot160\ 219$ aJ,   Å $= 10^{-10}$ m.

(a) Ref. 35, (b) Ref. 36, (c) Ref. 38, (d) Ref. 39, (e) Ref. 37.

Table 1.   Semi-empirical EXH, IEXH and INDO, and Hartree–Fock *ab initio* calculations together with experimental data on N_2.

3. METHODS OF COMPUTATION OF GROUND STATE POTENTIAL

The three LCAO methods are used first to compute the anisotropic inter-molecular potential between pairs of nitrogen molecules, by solving the electronic eigenvalue problem of two molecules that are regarded as a single 'super-molecule' and calculating the total electronic energy as a function of distance and orientation of its molecular constituents.   Following a similar approach of De Boer [40] on H_2–H_2 interaction, the resultant potential is numerically fitted for convenience of further computations, to some analytical form of anisotropic non-bonded atom–atom interaction in a small distance range in the vicinity of the crystalline intermolecular equilibrium separation.   Since closed shell SCF-MO calculation without configuration interaction gives no dispersion attraction forces [5, 41], the atom–atom potential functions chosen for fitting the LCAO results were taken to be of the repulsive $\phi_1 = \sum_{i=1}^{4} A/r_i^{12}$ or $\phi_2 = \sum_{i=1}^{4} (B/r_i^{12} + C/r_i^9)$ forms.   The former potential function was previously successfully employed for representing the non-dispersive part of a phenomenological potential for $\alpha - N_2$ [3].   Both forms include a 'pseudo quadrupole–quadrupole' interaction potential (with the classic electrostatic quadrupole–quadrupole angular dependence and with a different radial behaviour), as can be best viewed by expanding

these analytical forms in products of spherical-harmonics [42]. The five standard orientations used in this work for discussing properties of dimers (see § 7, 8) are displayed in figure 1. The orientations chosen for performing the calculation of the LCAO interaction energy, for fitting an atom–atom potential of the above forms, were obtained by sampling the entire range of spherical coordinates θ, ρ, which determine the mutual orientation of a given pair of molecules [43]. The mesh of this sampling was chosen to obtain stability of the standard deviation of the fit as a function of the number of orientations employed. The intramolecular equilibrium length was preserved at the value that was yielded by the corresponding semi-empirical method for an isolated molecule, since the experimental bond length in $\alpha - N_2$ crystal at normal pressure is only negligibly changed when compared with the gas phase experimental bond length. With this procedure, both forms of the potential ϕ_1 and ϕ_2 could be fitted in the range of intermolecular separation of $3 \cdot 5$ Å $\leqslant R \leqslant 4 \cdot 2$ Å with a similar average accuracy of 5 per cent for the EXH calculation and 9 per cent for the IEXH potential. The total intermolecular potential V_{ij} was calculated by adding the non-dispersive atom–atom potential thus calculated to the classic anisotropic dipole–dipole dispersion potential with standard parameters [1, 44], yielding finally the potential that is used in computing dynamical properties of α and γ nitrogen lattices.
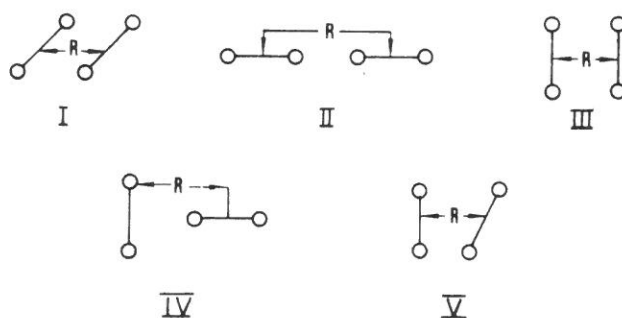

Figure 1. Dimer orientations.

For discussion of intermolecular bonding effects in the solid, another approach was adopted. A cluster made up of one N_2 molecule surrounded by successive shells of first and second molecular neighbours ($1 + 12 + 6$ molecules respectively), arranged mutually in their crystalline configuration, was treated as a 'supermolecule' and its all-valence electron eigenvalues were computed in the IEXH charge self consistent method as a function of molar volume thus allowing for charge redistribution effects to take place. Intermolecular bond formation and non-additivity deviations of the former two-molecule model, were examined.

The description of the non-dispersive part of the intermolecular interaction in the solid by overlap-including all valence electron semi-empirical molecular orbital methods (EXH, IEXH), although crude from the point of view of the approximations inherent to these quantum mechanical methods, is advocated for several reasons. The automatic inclusion of orthogonality corrections which play a significant role in determining intermolecular forces, and the fact that these methods allow for the formation of intermolecular bonding, which was shown to be an effective mechanism in stabilizing some molecular crystals, [4, 5] favour

their use. The favourable results obtained in the calculation of molecular quadrupole moments of a large number of molecules [46] from IEXH wave functions, indicate that quadrupole–quadrupole interactions should be reasonably reproduced by molecular cluster calculation employing these wave functions. Also the inclusion of all overlap integrals, which are important in determining the intermolecular end-to-end repulsion and relative end-to-centre attraction, suggest that these methods should furnish a reasonable starting point to construct intermolecular potentials from cluster wave functions.

4. RESULTS FOR GROUND STATE POTENTIAL

The results for the intermolecular potential, calculated by the three LCAO methods, for two selected orientations (similar behaviour was obtained in most of the examined orientations) are shown in figure (2 *a*) and 2 (*b*) together with the non-dispersive part of the phenomenological potential of Kuan, Warshel and Schnepp [3]. The authors obtained the two potentials by correlating the lattice mode frequencies with the crystal energy and nearest neighbour distance, via a parametrized pair potential. Recently, Suzuki and Schnepp [4] have shown that the specific heat of solid $\alpha - N_2$ can be calculated in good agreement with experiment from this potential. These authors have also shown that this potential model gives reasonable results for the second virial coefficient of N_2. It is evident by inspection that the IEXH and EXH potentials agree reasonably with the phenomenological one, while the INDO potential underestimates it markedly. At intermediate and long intermolecular distance, all three calculated potentials underestimate the phenomenological interaction, in line with the well known tendency of Slater atomic functions to decrease the interaction matrix elements at these distances [48]. The INDO procedure, based on zero differential overlap on the one hand, and describing poorly molecular quadrupole moments [49] on the other, results in a potential that deviates strongly from both the EXH and IEXH as well as from the phenomenological potentials. The neglect of intermolecular overlap in this procedure also causes the intermolecular potential for the D_{2h} configuration (3 in figure 1) to vanish due to symmetry.

Covalent bond formation between non-bonded atoms was suggested to take place in the halogen crystal stabilization process [4, 45]. This possibility was tested in the N_2 crystal by performing a cluster calculation by IEXH method of one molecule surrounded by its 12 nearest neighbours and another calculation of one molecule surrounded by its 12 nearest neighbours plus 6 next nearest neighbours. The intramolecular bond population of the central molecule was found to change by less than 10^{-2} per cent from its free molecule value in these clusters, and the bond population between non-bonded atoms in nearest neighbour molecules was found to vary from $-15 \cdot 4 \times 10^{-4}$ for a unit cell dimension of $5 \cdot 40$ Å, to $-3 \cdot 6 \times 10^{-4}$ for a unit cell of $6 \cdot 0$ Å. This slight antibonding character of the end-to-end interactions between molecules is thus small in the Pa3 structure of N_2.

Non-additivity of the interaction energy per molecule was calculated by comparing the interaction energy in the cluster calculation, with that obtained by summing the appropriate pair interactions. It is found to be less than 1 per cent in this calculation for the largest cluster considered, in accord with the negligible intermolecular bond formation and small charge redistribution in the cluster
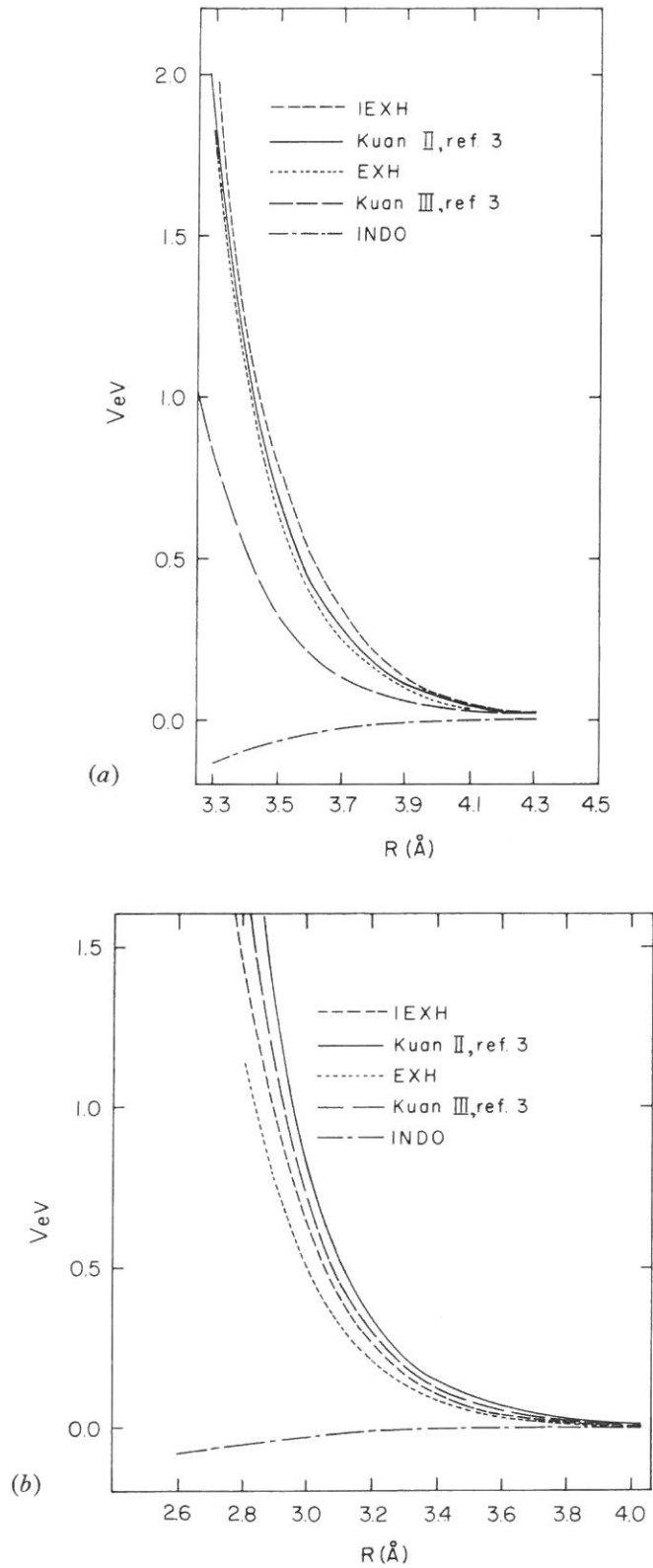
Figure 2. Dimer interaction potentials calculated according to the phenomenological potentials of Kuan *et al.* [3] and IEXH, EXH and INDO theories. (*a*) Linear configuration. (*b*) Perpendicular in-plane configuration.

environment as compared with free molecule values. To test the quality of the potentials and that of the cluster approach employed, several properties of α and γ nitrogen crystals were computed. The static crystal interaction energy was computed for both α and γ forms and compared with the values obtained from the phenomenological potential. This was done by using as an analytical pair potential the LCAO interaction in its atom–atom ϕ_1 form plus the dispersion contribution. The constant A obtained by fitting the LCAO energy of inter-action in the range of $3.5\ \text{Å} < R < 4.2\ \text{Å}$ was 5.21863×10^5 and 5.31710×10^5 kcal Å^{12}/molecule for EXH and IEXH calculations, respectively. The crystal interactions were summed over 5^3 unit cells, and the unit cell vectors a, b and c were varied independently to yield the absolute minimum in the potential energy under the conditions of uniform stress by efficient steepest descent and Newton–Raphson methods [50]. The results for IEXH and EXH potentials are sum-marized in table 2 together with experimental results, and the values obtained from the phenomenological potential 2 of Kuan, Warshel and Schnepp. For comparison, the unit cell dimensions of both $\alpha - N_2$ and the $\gamma - N_2$, and the static energy, that were not described by these authors, was computed from their potentials.

The INDO potential revealed unreasonably large negative energy values, and it was therefore decided at this stage that this method is inadequate for

Property	Phenomeno-logical potential (a)	Experiment	IEXH	EXH
$\alpha - N_2$ form :				
a, b, c/Å	$a=b=c=5.62$	$a=b=c=5.66$ (b)	$a=b=c=5.41$	$a=b=c=5.56$
E_{static}/(kcal/mole)	-1.81	—	-1.95	-1.99
Translation modes :				
$v(A_u)$/cm^{-1}	46.6	Inactive	37.5	39.5
$v(E_u)$/cm^{-1}	53.3	Inactive	49.7	46.7
$v(T_u)$/cm^{-1}	49.4	48 ± 1 (c)	45.4	42.9
$v(T_u)$/cm^{-1}	73.4	69 (c)	65.9	61.3
Libration modes :				
$v(E_g)$/cm^{-1}	36.1	31.5 (d)	33.4	31.8
$v(T_g)$/cm^{-1}	40.7	36.0 (e)	37.5	35.6
$v(T_g)$/cm^{-1}	49.6	59.8 (c)	44.9	42.9
$(E_{\text{static}}+E_{\text{z.p}})$/(kcal/mole)	-1.502	-1.658 (f)	-1.670	-1.626
$\gamma - N_2$ form :				
a, b, c/Å	$a=b=4.12$ $c=5.31$	$a=b=3.957$ $c=5.109$ (g)	$a=b=4.09$ $c=5.17$ (h)	$b=4.12$ (h) $c=5.09$
E_{static}/(kcal/mole)	-1.76	—	-1.91	-1.99

kcal $= 4.184$ kJ,   atm $= 101\ 325$ Pa.

(a) Ref. 3   (e) Ref. 24
(b) Ref. 21   (f) Ref. 23
(c) Ref. 28   (g) Ref. 22, at 3500 atm
(d) Ref. 26   (h) Calculated for internal pressure of 3500 atm

Table 2. Summary of ground state calculations for α and γ nitrogen crystals.

stability calculations in closed shell systems. Similar conclusions as to the inadequacy of the INDO method for describing ground state energy properties of bonded interactions in atomic crystals had been previously reached by others [10, 51].

The agreement between calculated and experimental unit cell dimensions is of the order of 5 per cent for the α form, and 2 per cent for the γ form, the IEXH results being slightly better than EXH results.

The $\gamma - N_2$ phase was found to have less static internal energy than the α-phase by 0·05 kcal/molecule and 0·04 kcal/molecule using the phenomenological and IEXH potentials, respectively. The ratio c/a for the γ phase is close to the experimentally measured value of 1·29 [22], being 1·288 and 1·264 for these two potentials, respectively.

5. LATTICE MODE FREQUENCIES

The lattice modes of $\alpha - N_2$ were calculated by standard procedures [2] by diagonalization of the eigenvalue problem defined by the force constant matrix which is evaluated from the atom–atom potentials. Again 5^3 unit cells were included and the $\tilde{q} = 0$ modes evaluated. These results together with experimental data and the frequencies calculated by potential 2 of Kuan et al. are summarized in table 2.

The potentials obtained by the IEXH method yield results for translation and libration frequencies that deviate from experimental results by an average of 3 cm^{-1} and 6 cm^{-1}, respectively, while the corresponding deviations for EXH potentials are 7 cm^{-1} and 6 cm^{-1}, respectively. Both methods fail mainly to reproduce the high T_g librational frequency correctly. Such a discrepancy was previously obtained by other authors and was treated by introducing a third adjustable parameter, i.e. the bond length in the work of Kuan et al. [3] and the quadrupole moment in the work of Anderson et al. [24].

The deviation from experimental results obtained with these potentials should be compared with other results : Goodings and Henkelman [52], Jacobi and Schnepp [53] and Raich [54] employed a pure quadrupole–quadrupole potential, and obtained a mean deviation of 8·5 cm^{-1}. Goodings and Henkelman [52] employ anisotropic dispersion interaction together with a quadrupole term and a parametrized repulsive potential obtained a mean deviation of 29 cm^{-1}. The parametrized atom–atom potential of Donkersloot and Walmsley [2] yielded a mean deviation of 12 cm^{-1} and 6 cm^{-1} for libration and translation frequencies, respectively. The 6–12 atom–atom potential presented recently by Jacobi and Schnepp [55] yields an average deviation of 4 cm^{-1} and 6 cm^{-1} for translational and librational modes, respectively.

It should be noted that when the total energy (static + zero point energy, ZPE) is calculated for different molar volumes both for α and γ phases (by solving the dynamical problem at each volume and thus calculating the ZPE) this potential fails to reveal a phase transition between these phases, and the α-form is the most stable in the range of molar volumes from 20 to 27 cm^3/mol. The smallest difference in total energies, between these phases, is 0·1 kcal/mole at $V = 23·5$ cm^3 which is only 8 per cent from the total energy of the α-phase at this volume. Non-additivity corrections and the deviation from harmonic behaviour, should be important in studying such small differences in energy. The

inability of various atom–atom potentials as well as the Khoin potential [1] to reveal the α–γ phase transition has been previously discussed, whereas a parametric shape dependent hard core interaction could explain this transition [56]. Unfortunately this potential has never been examined regarding its capability of explaining the solid lattice vibrations.

The zero point energy of $\alpha - N_2$ was next evaluated from the $\tilde{q} = 0$ calculated optical lattice modes by assuming a small dispersion in the optical branch, each mode being weighted according to its degeneracy, and neglecting the contribution of the acoustic branch. This is justifiable in view of the weak dispersion of the optical branch and the very small density of states in the energy region corresponding to the acoustic phonons, as exhibited in the detailed dynamical calculation of Ron and Schnepp [57]. The error introduced by these assumptions was estimated† to be approximately 20 per cent of the total zero point energy. The zero point energy thus calculated by the IEXH method is 0·280 kcal/mole, that calculated by the EXH method is 0·264 kcal/mole while the phenomenological potential yields 0·308 kcal/mole and a simple Debye model with $\theta_D = 68°$ [58] yields 0·151 kcal/mole. Adding the ZPE to the static potential, we obtain the crystal cohesion which is given in table 2 together with the experimental value. The deviation from experiment is 12 per cent in EXH calculation and 10 per cent in IEXH calculation.

The effect on the unit cell dimension introduced by minimizing the total electronic plus optical zero point energy, instead of the electronic energy alone, was checked by performing a variational calculation on this total energy. Calculations with IEXH potential reveal that the minimum in total energy now occurs at $a = b = c = 5·50$ Å for the α phase and $a = b = 4·12$ and $c = 5·25$ in the γ phase.

6. Davydov splitting of Π_g state in $\alpha - N_2$

We next consider the electronic Davydov splitting in the $\alpha - N_2$ crystal arising from the lowest molecular excitation $X^1\Sigma_g^+ \rightarrow a^1\Pi_g$. The N_2 molecules occupying the four sites in the Pa3 unit cell give rise to a totally symmetric A_{1g} crystal ground state and to the $\tilde{k} = 0$ exciton states belonging to the irreducible representation $F_{1g} + F_{2g} + E_g$ of the factor group T_h. The transition from the ground state to the doubly degenerate E_g state is forbidden, while the transitions to the F_{1g} and F_{2g} states are allowed by electric quadrupole and magnetic dipole. The overall splitting between these states was measured in the u.v. spectrum of $\alpha - N_2$ by Brit and Schnepp [29] and by Dressler [30] as 1000 cm^{-1}. The former authors also calculated the splitting by considering transition quadrupole interactions only and fitting the observed splitting by a quadrupole oscillator strength treated as an adjustable parameter. This yielded an oscillator strength for the electronic transition 3 times smaller than the experimental value, and an overestimation of the polarization ratio by a factor of 5.

It was previously demonstrated that resonance interactions between transition multipoles in the interacting molecules, fail entirely to reproduce the experimental spectral shifts [29] and that overlap must be introduced explicitly to account for the shift and splitting in the excited state [59]. A direct molecular orbital

† Either by considering a Debye model for the acoustic branch with an acoustic θ_D taken to be smaller or equal to the lowest optical frequency, or by evaluating directly from the dynamical calculation [57]

approach which introduces automatically exciton and charge-resonance effects [20] and enables minimization of internal degrees of freedom corresponding to excited state configuration, should be a more adequate method for calculating energies and spectral shifts in molecular crystals. As a further check on the applicability of the semi-empirical molecular potentials to non-bonded interactions, the Davydov splitting of this transition was calculated from a cluster model by a direct molecular orbital approach.

The energies of the F_{1g} and F_{2g} exciton states are related to the interaction matrix elements over the free molecule wave functions $\phi_{ip}{}^0$, $\phi_{ip}{}^\alpha$ and $\phi_{ip}{}^\beta$, where i is the site occupied by the molecule in the unit cell, p is the index of the unit cell and 0, α and β represent the ground and the two orthogonal components of the molecular degenerate state respectively, by

$$E_{1,\,2} = \Delta\omega + \tfrac{1}{2}(D_\alpha + D_\beta) + \tfrac{1}{2}(F_{\alpha,\,\alpha} + F_{\beta,\,\beta}) \pm \tfrac{1}{2}\{(F_{\alpha,\,\alpha} - F_{\beta,\,\beta})^2 + 4F_{\alpha,\,\beta}{}^2\}^{1/2} \qquad (1)$$

where $\Delta\omega$ is the free molecule excitation energy, and the first order contribution to the spectral shift D is given by $\tfrac{1}{2}(D_\alpha + D_\beta)$ where

$$D_\alpha = \sum_q{}' \langle \phi_{ip}{}^\alpha \phi_{iq}{}^0 | V_{ip,\,iq} | \phi_{ip}{}^\alpha \phi_{iq}{}^0 \rangle$$

$$- \langle \phi_{ip}{}^0 \phi_{iq}{}^0 | V_{ip,\,iq} | \phi_{ip}{}^0 \phi_{iq}{}^0 \rangle = \sum_q{}' d_{pq}{}^{\alpha 0} \qquad (2)$$

$V_{ip,\,iq}$ is the interaction pair potential and the primed sums omit the term where $p = q$. The $F_{\alpha,\,\beta}$ terms are related to sums over the four sublattices $I = 1 \ldots 4$ by

$$F_{\alpha,\,\beta} = \sum_{I=1}^{4} C_I M_{1,\,I}{}^{\alpha,\,\beta} \qquad (3)$$

$$M_{i,\,j}{}^{\alpha,\,\beta} = \sum_{q=1}^{N/4} \langle \phi_{ip}{}^\alpha \phi_{iq}{}^0 | V_{ip,\,jq} | \phi_{jq}{}^\beta \phi_{ip}{}^0 \rangle = \sum_q^{N/4} I_{ip,\,jq}{}^{\alpha,\,\beta} \qquad (4)$$

where the reference molecule is labelled by i. N is the number of molecules and C_I are the expansion coefficients of the exciton states in terms of one site excitation functions corresponding to the $\tilde{K} = 0$ representation of the factor group states F_{1g} and F_{2g}. The Davydov splitting between the F_{1g} and F_{2g} states is given by twice the last term in equation (1), while the shift of the centre of the crystal band relative to the free molecule transition is given by the second and the third term in equation (1).

When pure quadrupole–quadrupole interaction is assumed, the summation in equation (4) over next nearest neighbours was shown to contribute less than 1 per cent to the total splitting, and interaction between translationally equivalent molecules does not contribute to it [29]. Thus a single unit cell weighted by its appropriate number of nearest neighbours makes the largest contribution to the splitting. The crystal Davydov splitting was therefore constructed from the solution of the unit cell LCAO problem employing orthogonal $1s$, $2s$, $2p_x$, $2p_y$ and $2p_z$ functions per atom (a total of 40 atomic orbitals), the molecular equilibrium length obtained by minimizing the ground state energy of a single molecule and the unit cell equilibrium dimensions.

The spectral shift of the centre of the absorption band in the crystal relative to the free molecule transition is calculated by relating the spectral shift $R_{1,\,J}$ of a pair of molecules 1 and J to the crystal shift R_c via

$$R_{1,\,J} = \tfrac{1}{2}(I_{1,\,J}{}^{\alpha\alpha} - I_{1,\,J}{}^{\beta\beta}) + \tfrac{1}{2}(d_{1,\,J}{}^{\alpha,\,0} + d_1{}_J{}^{\beta,\,0}) \tag{5}$$

$$R_c = \sum_J^N R_{1,\,J} \tag{6}$$

The dimer spectral shift is obtained from the solution of the LCAO problem for two N_2 molecules mutually oriented as a given pair in the crystal, and the summation in equation (6) is carried out for three orders of neighbours.

Finally, the additivity of the model was checked by performing a cluster calculation, i.e. directly solving the eigenvalue spectrum of a cluster consisting of one molecule surrounded by 12 non-equivalent and 6 equivalent nearest neighbours arranged according to the Pa3 structure. The eigenvalues obtained were analysed to yield the red shift of the centre of the band. The results for the splitting and spectral shift are summarized in table 3 together with the experimental data. Agreement with the experimental Davydov splitting is good while the result for the first order red shift seems to be too high since the second order contribution to R_c is expected to be important, in view of the large change in intramolecular bond length during excitation. The cluster model calculated by the EXH method yields a mean red shift of the origin of the band of -210 cm^{-1}, suggesting that additivity corrections to the splitting are not large. The close agreement obtained between the results of a single unit cell and larger cluster calculations, suggest that surface effects have only a small influence in the former case. This is unlike the situation met in atomic clusters like diamond [11], boron nitride [10 a] and graphite [10 b] where the presence of 'unsaturated' *bonded* interactions strongly perturbs the cluster states.

	IEXH	EXH	Adjusted quadrupole moment [29]	Experimental
Total splitting/cm^{-1}	936	739	1000	1000, Refs. 30, 29
Red shift/cm^{-1}	-197	-220	-40†	-270, Ref. 29
				-170, Ref. 30

† Contribution of the quadrupole exchange term between translationally equivalent molecules : $\tfrac{1}{2}(F_{\alpha\alpha} + F_{\beta\beta})$.

Table 3. Davydov electronic splitting and red shift for $\alpha - N_2$

When the calculation is repeated for different unit cell dimensions $\bar{a}$, the splitting is shown to depend on this parameter as $a^{-11\cdot6}$ for EXH calculation and $a^{-12\cdot0}$ for IEXH calculation in the range $5\cdot7 \leqslant a \leqslant 5\cdot55$ Å. The similarity in the distance dependence is expected, since charge self-consistent redistribution accounted for in IEXH procedure is not as important in homonuclear systems in determining energy band differences as in heteronuclear systems where IEXH yields a higher dependence than EXH [12]. The distance dependence obtained

here for the splitting is remarkably shorter range than that expected from quadrupole interactions only. The rapid convergence of the crystal sums due to this short range potential simplifies this calculation greatly and is probably the main reason for the compatibility of the cluster calculation.

Crystal field mixing with the F_g exciton components of the free molecule Δ_g state is expected to be negligible in view of the weakness of the transition to the latter in the free molecule, allowed only by electric quadrupole.

7. NITROGEN MOLECULAR ION INTERACTIONS

Nitrogen ground state molecule-molecular ion ($N_2 - N_2^+$) interactions were studied extensively in the past years using mass spectrometry in glow discharge, electron beam experiments, afterglow experiments and mobility measurements (Ref. 31 and Refs. 1–14 cited therein). The enthalpy of formation of $N_2 + N_2^+ \rightarrow N_4^-$ was determined to be 11·3 kcal/mole at 1000°K [32] and due to the small intermolecular vibrations [59] this is also approximately the static binding energy. The change in ionization potential in going from N_2 to N_4 clusters was measured to be $0·5 \pm 0·1$ eV [31]. The intermolecular arrangement that yields a minimum in energy could not be anticipated from experiment.

The binding energy of this complex (due to charge-quadrupole and charge-atomic polarization effects), is much higher than the valence and van der Waals binding in the neutral closed shell $N_2 - N_2$ pair. Earlier CNDO/2 calculations [16] were unsuccessful in predicting this binding, and $2S_A - 2P_A$ type integrals and intermolecular overlap corrections were introduced to the theory to account for these effects. Three adjustable parameters were used to account for the excessively negative quadrupole moment yielded by neglecting intramolecular overlap, and to fit the O_4^+ data. The O_4^+ binding energy was thus calculated to be within 8 per cent of the experimental value, while the corresponding deviation for O_4^- and N_4^- was 20 per cent and 200 per cent, respectively.

The fact that EXH and IEXH theories automatically include intra- and intermolecular overlap, the latter accounting self-consistently for charge redistribution from one and two centre contributions, suggests their use in constructing molecular ion interactions. The clear advantage of the improved CNDO procedures is in the explicit treatment of open shell states.

The N_4^+ cluster was treated by EXH and IEXH methods with the previously determined atomic orbital energies, for configurations 1–5 shown in figure 1. The energies and intermolecular distances at equilibrium for these arrangements are summarized in table 4. The linear configuration is shown to be the most

Con- figuration	EXH		IEXH		Conway [16]		Experi- mental binding (kcal/mole)
	Distance (Å)	Maximum binding (kcal/mole)	Distance (Å)	Maximum binding (kcal/mole)	Distance (Å)	Maximum binding (kcal/mole)	
2	3·8	4·8	3·7	8·8	3·1	34·70	11·5
3	3·3	1·15	3·3	0·2			
5	3·4	0·55	3·4	~0·1			
4	3·8	0·32	3·7	0·7			
1	3·4	0·022	3·3	0·02			

Table 4. Binding energy of $N_2 - N_2^+$ for the configurations shown in figure 1.

stable one, as suspected earlier [58] and predicted by the calculations of Conway [16]. The decrease in ionization potential in going from N_2 to N_4 is calculated to be 0·41 eV by EXH and 0·60 eV by IEXH methods, as compared with the experimental value of $0·5 \pm 0·1$ eV [31]. The EXH method accounts for only 42 per cent of the binding energy, while the IEXH method is somewhat better, accounting for 76 per cent of the binding. Open shell treatment with inclusion of exchange interactions should probably be applied if more accurate results are sought.

8. Excimer formation

The extended Hückel method was previously employed [14, 15, 58 *a, c*] for excimer stability calculations in aromatic organic systems, where semi-qualitative agreement with the observed excimer fluorescence and ground state repulsion was obtained. The fact that this procedure accounts for intermolecular over-lapping and charge resonance states essential for the description of excimer stability was argued to be the main reason for its adequacy. Iterative procedures such as IEXH were shown to be superior to the non-iterative methods because of their greater ability to account for ionic states via self-consistent charge distribution.

The possibility of nitrogen excimer formation is considered here by calculat-ing the excimer stability energy D by EXH, IEXH and INDO methods for configurations 1–5 in figure 1. The molecular excited state II_g of the separated N_2 molecules splits in the general dimer configuration into 4 states, the lowest of which is capable of stabilizing an excimer state. In the linear $D_{\infty h}$ configuration (II in figure 1), the molecular degeneracy is preserved on forming a dimer (the excimer states generated transform like $E_1 + E_2$), while in configurations 4 and 5 it is partially removed (representation $E + A + B$) and in configurations 1 and 3 it is completely removed (representations $A_1 + A_2 + B_1 + B_2$). The excimer stabilization energies resulting from each of the lowest components of these states in the five configurations are listed in table 5. The agreement in equilibrium excimer separation as calculated by EXH and IEXH methods is good, the latter yielding consistently higher stabilization energies. INDO calculations did not reveal an excimer bound state but yielded instead dissociative states for all the configurations that were studied. This is probably due to the neglect of overlap which is essential in excimer stabilization. More detailed calculations on these excimers do not seem to be justified at this stage when experimental data are unavailable.

Configuration	$R_{min}/\text{Å}$		D/eV	
	EXH	IEXH	EXH	IEXH
1	3·0	2·9	−0·32	−0·37
2	3·6	3·6	−0·29	−0·43
3	2·5	2·4	−0·27	−0·33
4	3·3	3·3	−0·10	−0·17
5	3·4	3·4	−0·003	−0·11

Table 5. Nitrogen excimer stability (D) for different configurations calculated by EXH and IEXH methods.

9. Summary and conclusions

EXH, IEXH and INDO semi-empirical LCAO methods were examined as possible methods for constructing non-bonded potentials. The reasonable agreement obtained for the ground and excited state properties of nitrogen crystals and small nitrogen clusters, together with the favourable results obtained previously for Cl_2–Cl_2 ground state interaction [45] by EXH and O_2–O_2 interaction using improved CNDO/2 methods [16], suggest that these methods could serve as a reasonable starting point for constructing semi-quantitative potentials from molecular wave functions. The IEXH method is probably the most suitable, for it has the gross features needed to describe the crystal potential, i.e. it has full overlap interaction, predicts the approximate magnitude of quadrupole moments in the free molecule, contains orthogonality corrections over different centres and it self-consistently treats charge transfer and redistribution over the cluster. It should however be stressed that only semi-quantitative results can be expected from such procedures and if more accurate results are required, *ab initio* methods cannot be avoided. Alternatively, the IEXH scheme can be used as a starting iteration in a refinement procedure which varies the atomic orbital energies and orbital exponents requiring maximal agreement between several observables and the calculated intra- and intermolecular properties. The results obtained here for the particular example of nitrogen are encouraging in this respect.

The computations were carried out on the CDC 6600 computer at the Tel Aviv computer centre, and on the IBM 370 at the Weizmann Institute, Rehovoth.

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