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The electronic structure of the tetrahedral N_2 centre and of the neutral vacancy in diamond

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Abstract. The N_2 centre, a tetrahedral array of four F centres, and the neutral vacancy in diamond present similar theoretical problems. Their electronic structure has been calculated by a molecular orbital approach using one-electron wave functions centred on the geometric centre of the defect. The results are compared with those based on functions which are linear combinations of atomic orbitals (LCAO). We conclude that in LiF and KCl the ground state of the N_2 centre is $^5A_2$ and the centre is *not* responsible for the N_2 band, although it should give rise to spin resonance. For the diamond vacancy the ground state is $^3T_1$ or possibly ^1E. Previous calculations using LCAO wave functions give a ^1E ground state for diamond. Possible ways of observing these centres are discussed.

1. Introduction

Pick (1960) suggested that aggregates of F centres were responsible for a number of the optical absorption bands in alkali halide crystals. In particular, he proposed that the centre which gave rise to the N_2 band, which has been seen at 5400 Å in LiF and at 10 500 Å in KCl (Compton and Rabin 1964), consisted of four F centres arranged tetrahedrally on adjacent sites. Pick's model is shown in figure 1. The resulting centre, consisting of four 'defect electrons' localized on four anion vacancies, is electrically neutral, so the crystal lattice will be nearly perfect except in the vicinity of the defect. The four anion vacancies leave behind a tetrahedral array of four positive ions (the 'defect ions'), and it is convenient to consider the centre as four defect electrons localized near the defect ions. Although no experimental work has satisfactorily identified the N_2 bands with the centre under discussion, we shall continue to refer to this model as the N_2

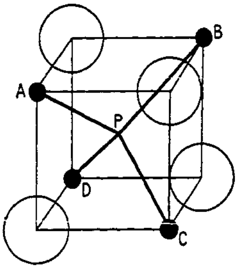

Figure 1. The N_2 centre. The four defect ions are denoted by the small closed circles and the negative ion vacancies by the large open circles. The defect ions, A, B, C, D, are all distance R from P. The four defect electrons are not indicated.

centre. In the present paper we calculate the electronic structure and energy levels of the N_2 centre for several crystals. No attempt is made to calculate the stability of the centre, i.e. we calculate relative rather than absolute energies throughout.

It is shown in § 3 that the properties of the defect electrons are almost entirely determined by the defect ions—the rest of the lattice fixes the defect ion positions, but otherwise has little effect. The electronic structure of the centre can thus be determined by a molecular orbital calculation. The choice of one-electron molecular orbitals for the defect electrons is discussed in § 2. The four-electron wave functions are limited by the Pauli exclusion principle, and for these we adopt linear combinations of Slater determinants with the required spin and symmetry. The calculation of the electronic energy levels is then that of solving the appropriate secular equations, in which the total Hamiltonian includes the interaction between the defect electrons as well as their kinetic energy and potential energy of interaction with the lattice. Configuration interaction is included completely in solving these secular equations.

The present calculation is related to the calculations of the electronic structure of the neutral vacancy in diamond (Coulson and Kearsley 1957, Yamaguchi 1962). In the diamond lattice each atom is covalently bonded to its four neighbours, which are arranged tetrahedrally around it. The removal of an atom breaks the four bonds to its neighbours, and the four electrons of the neighbours which previously contributed to these bonds are analogous to the defect electrons of the N_2 centre. Certain features of the work on diamond carry over directly to the present case. Thus the four-electron wave functions are written in terms of the one-electron functions in the same way, and secular equations have the same form. On the other hand, the appropriate one-electron molecular orbitals differ and the potentials in which the defect electrons move are different. For the alkali halides the perfect lattice is a cubic array of positive and negative ions, and the defect ions are positive ions, whereas in diamond the perfect lattice is non-polar, being a tetrahedral array of covalently bonded atoms, in which the analogues of the defect ions are covalently bonded to the rest of the lattice. The calculations here concentrate on the cases of the alkali halides LiF and KCl, the two cases in which the N_2 centre has been tentatively identified (Compton and Rabin 1964). Results are also given for the vacancy in diamond, and, although these must be treated with reserve, they verify some of the conclusions of the previous calculations and shed some light on the differences between the results of Coulson and Kearsley and those of Yamaguchi.

In § 2 we discuss the electronic wave functions. Two forms of one-electron molecular orbital are considered, the linear combination of atomic orbitals (LCAO) and one-centre wave functions centred on the geometric centre of the defect. The latter form is the most useful for the N_2 centre. The parameters which describe the radial dependence of the one-centre functions are calculated self-consistently in § 3 for a particular analytic form of the radial dependence. The potential appropriate to the N_2 centre is also discussed in this section. The electron–electron interaction integrals are evaluated in § 4, where the great advantage of one-centre functions is apparent, as the integrals can be calculated analytically rather than in terms of the approximate many-centre integrals necessary with LCAO wave functions. The secular equations are solved in § 5 to give the energy levels, and the effects of varying the parameters used are considered. Where comparison is possible the LCAO and one-centre function approaches give essentially the same results. Finally, the experimental consequences of this work are discussed. Our calculations suggest that the N_2 centre is not responsible for the N_2 band, as transitions of suitable energy from the ground state are forbidden by the spin selection rule. The N_2 centre should give rise to a spin resonance signal, as its ground state is predicted to be $^5A_2$.

2. The electronic wave functions

The N_2 centre is illustrated in figure 1. We label the four defect ions A, B, C, D, which are all a distance R from the geometric centre P of the defect. In the LCAO picture the one-electron molecular orbitals are combinations of the atomic orbitals a, b, c, d (centred on A, B, C, D respectively) which transform correctly under the symmetry group T_d of the defect. These are

$$v' = \frac{a+b+c+d}{(1+3S)^{1/2}}$$

which forms a basis for the representation A_1, and

$$t_x' = \frac{a+b-c-d}{(1-S)^{1/2}}$$

$$t_y' = \frac{a-b-c+d}{(1-S)^{1/2}}$$

$$t_z' = \frac{a-b+c-d}{(1-S)^{1/2}}$$

which form a basis for the representation T_2 of T_d. In these $S = \langle a|b\rangle$ is the overlap between the atomic orbitals. When S is large it is more appropriate to use wave functions centred on P. If r is the distance from P, then corresponding one-centre functions are

$$\begin{aligned} v &= R_v(r)\left(1+\gamma\frac{xyz}{r^3}\right)\left(1+\frac{\gamma^2}{105}\right)^{-1/2} \\ t_z &= R_t(r)\left(\frac{xy}{r^2}+\delta\frac{z}{r}\right)\left(\frac{1+5\delta^2}{15}\right)^{-1/2} \end{aligned} \qquad (1)$$

with similar expressions for t_x and t_y. The angular terms are the simplest terms of the correct symmetry with even and odd parity respectively. Both parities are necessary, as the centre does not have inversion symmetry.

The atomic orbitals a, b, c, d are usually taken to be a linear combination of an s orbital and a p orbital symmetric about the axis joining the atom in question to P. The corresponding atomic radial functions are conveniently given by the approximate analytic forms due to Slater (1930)—if r_i is the distance from atom i these radial functions have the form $r_i^n \exp(-cr_i)$. Clearly $\exp(-cR)$ is a measure of the overlap of the atomic functions, although the overlap also depends on the relative fractions of s and p orbitals, for example. For diamond, LiF and KCl respectively $\exp(-cR)$ is 0·082, 0·323 and 0·237. Whilst it is reasonable to use a LCAO function for diamond the overlap is much larger in the other two cases, where the one-centre functions are more appropriate.

A comparison of the LCAO and one-centre functions suggests that for a first orientation $\gamma = 1/\delta = 0$ is a good choice for γ and δ. Thus if the atomic orbitals are a linear combination of s and p orbitals, as mentioned earlier, then the LCAO orbitals have the properties, irrespective of the details of the radial functions,

$$v'\left(r,\frac{\mathbf{r}}{r}\right) = +v'\left(r,\frac{-\mathbf{r}}{r}\right)$$

$$t'\left(r,\frac{\mathbf{r}}{r}\right) = -t'\left(r,\frac{-\mathbf{r}}{r}\right)$$

for $r = 0$ and $r = \infty$—thus for very small or very large r the v orbital has even parity and the t orbital odd parity. For the one-centre functions (1) this would imply $\gamma = 1/\delta = 0$, and these values will be adopted in most of the present calculations. Gourary and Fein (1962) used one-centre functions with this particularly simple angular form in a similar context, and we will refer to the case $\gamma = 1/\delta = 0$ as the GF limit.

The radial functions $R_v(r)$ and $R_t(r)$ adopted have the simple (unnormalized) form

$$\begin{aligned} R_v &\sim \exp\left(-\nu\frac{r}{R}\right) \\ R_t &\sim \exp\left(-\theta\frac{r}{R}\right) \end{aligned} \tag{2}$$

in which ν and θ are determined by a self-consistent calculation in § 3.

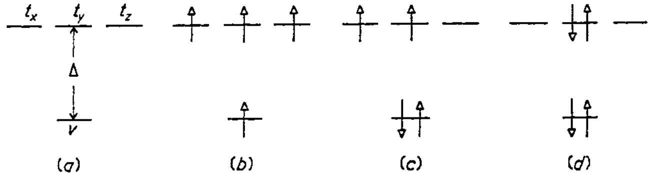

Figure 2. Schematic energy level diagram for the one-electron molecular orbitals: (*b*) illustrates the $^5A_2$ state, (*c*) the $^3T_1$ state and (*d*) a singlet state, such as ^1E.

The one-electron molecular orbitals are shown schematically in figure 2(*a*), in which the energy Δ is solely due to differences in electronic kinetic and potential energy. The four defect electrons can be put into the four molecular orbitals in a variety of ways. The exclusion principle reduces the number of possible configurations to three: (v^2t^2), (vt^3) and (t^4), where (v^nt^{4-n}) corresponds to n electrons in a molecular orbital of symmetry A_1 and $4-n$ electrons in orbitals of symmetry T_2. Suitable linear combinations of Slater determinants can be found for each configuration which form bases for the irreducible representations of T_d.

The methods of obtaining these four-electron wave functions have been described in detail by Coulson and Kearsley (1957), whose table 3 gives them in terms of the one-electron wave functions. Their discussion will not be reproduced here. We shall, however, single out three four-electron states (^1E and $^3T_1$ of v^2t^2, and $^5A_2$ of vt^3) for particular discussion, as in all cases one of these forms the ground state of the centre.

The defect electrons have parallel spins in the $^5A_2$ state shown in figure 2(*b*) and, by the exclusion principle, have orthogonal spatial wave functions. By avoiding each other they reduce the electron–electron interaction, which will favour this state energetically if the kinetic and potential energy terms (of order Δ) are small compared with the electron–electron interaction. Exactly these arguments lead to Hund's rules in the theory of atomic structure and to the weak field limit of ligand field theory. Analogy with the strong field limit of ligand field theory suggests a $^3T_1$ ground state, as in figure 2(*c*). An electron in a v orbital has lower potential and kinetic energy than one in a t orbital, and if this energy difference Δ is large the v^2t^2 configuration will be favoured rather than the vt^3 configuration. The t electrons in the $^3T_1$ state have parallel spins and, as outlined above, will tend to give the lowest energy when the interaction between defect electrons is large. By contrast the ^1E state has zero total spin, and provides an analogue of kinetic superexchange in antiferromagnetism (Anderson 1963). The antiparallel electron spins give orthogonal spin functions so that the spatial wave functions can overlap and spread out, thus reducing kinetic energy. The singlet state is favoured if the electron–electron interaction energy is small compared with the kinetic energy. This is shown schematically in figure 2(*d*). There are three singlet states within the v^2t^2 configuration. Coulson and Kearsley have shown that the ^{1}E state is the most stable of these.

Within the configurations which can be obtained from the molecular orbitals considered, the $^5A_2$ state is the only one with spin 2. There are therefore no allowed optical transitions between the $^5A_2$ state and the other states of this group. On the other hand, both the $^5A_2$ and $^3T_1$ states should give rise to spin resonance. The allowed optical transitions from $^3T_1$ are to those with the same spin and of A_2, E, T_1 or T_2 symmetry. The ^{1}E state has spin zero, giving no spin resonance, and has allowed optical transitions to states of T_1 or T_2 symmetry with the same multiplicity. Both the $^3T_1$ and ^{1}E states are orbitally degenerate. The Jahn–Teller theorem (Griffith 1961, p. 209) predicts that if such a state is the ground state the centre will distort, removing the degeneracy and giving a ground state of lower energy. In the present case suitable distortions for the $^3T_1$ state have E or T_2 symmetry, and for the ^{1}E state have E symmetry.

3. The potential and the parameters of the radial functions

Two basic assumptions will be made concerning the potential in which the defect electrons move. The first is the 'point ion' approximation in which the ions are regarded as point charges of the appropriate sign (Gourary and Adrian 1960). This has been used for F and M centres with some success, and it has proved a valuable starting point for more sophisticated treatments. For details we refer to the reviews by Gourary and Adrian (1960) and Gourary and Fein (1962). The second approximation is that only the spherically symmetric part of the potential need be considered. This has been successfully used in almost all cases in which the point ion model has been adopted, and it has been shown (Kübler and Friauf 1965) that for the F centre better results are obtained with only the spherically symmetric part of the potential than when other cubic terms are included. Further, if the potential of the defect ions is expanded in cubic harmonics it is found that the first, second and fifth terms are zero by symmetry and that the expectation values of the third, fourth and sixth terms tend to cancel over a wide range of δ and γ. It is plausible to expect the cancellation to continue beyond the sixth-order harmonics and that in any case the influence of such highly anisotropic terms would be small.

Each shell of ions outside the four defect ions contains equal numbers of positive and negative ions. It follows from the two approximations that the potential due to these is zero. The main influence of these ions is that they constrain the defect ions to remain close to their sites in a perfect lattice—thus R is not treated as a variational parameter, as it might be in a molecular calculation. The neglect of these ions may be justified more directly, as for each ion at $\mathbf{r}$ there is one of opposite sign at $-\mathbf{r}$. The potential due to the rest of the lattice has therefore predominantly odd parity and has a zero expectation value for wave functions of definite parity. In addition the potential is zero along the cube axes through the centre P of the defect. Coulson and Kearsley (1957) and Gourary and Fein (1962) have also justified the neglect of the rest of the lattice from the LCAO viewpoint. Their work shows that, as we are interested in relative rather than absolute energy levels, the exchange interaction of the defect electrons with those of the rest of the lattice may be neglected.

The expectation values of the sum of the potential and kinetic energies for the one-centre functions (1) are

$$\begin{aligned} v&: \quad \frac{1}{2}\left\{\frac{1+(25/105)\gamma^2}{1+(1/105)\gamma^2}\right\}\left(\frac{\nu}{R}\right)^2-\frac{4}{R}\{1-(1+\nu)\mathrm{e}^{-2\nu}\} \\ t&: \quad \frac{5}{2}\left\{\frac{3+5\delta^2}{1+5\delta^2}\right\}\left(\frac{\theta}{R}\right)^2-\frac{4}{R}\{1-(1+\theta)\mathrm{e}^{-2\theta}\} \end{aligned} \tag{3}$$

in atomic units. It is clear that the kinetic energy of the v electron increases enormously with γ, and for this reason it is plausible to make γ small, as in the GF limit.

The values of ν and θ in (2) are calculated by minimizing the total energy of the four electrons in the Hartree approximation with respect to these variables. In the calculation of ν and θ (but not elsewhere) we replace the electron–electron interaction term in the total energy by its value when the electronic charge distributions are averaged over angles. This approximation is used in Hartree's self-consistent field method (see, for example, Slater 1960, p. 213) and results in a considerable simplification. For each configuration (v^2t^2, vt^3 or t^4) the minimization of the energy with respect to ν and θ leads to two equations which are solved simultaneously to give the values of these parameters. Thus the one-centre functions are rather more flexible than the LCAO functions, for the LCAO functions are the same in each configuration, whereas the one-centre functions are chosen self-consistently within each configuration. Values of ν and θ are given in table 1.

Table 1. The values of ν and θ

Lattice	Configuration	ν	θ
Diamond	v^2t^2	1·378	0·610
(R = 1·54 Å)	vt^3	1·495	0·688
	t^4	—	0·755
LiF	v^2t^2	1·427	0·637
(R = 1·74 Å)	vt^3	1·527	0·714
	t^4	—	0·789
KCl	v^2t^2	1·445	0·776
(R = 2·62 Å)	vt^3	1·650	0·840
	v^4	—	0·910

In general, $\nu \sim 1\cdot5$ and $\theta \sim 0\cdot7$. With these values 92% of the v orbital charge and 51% of the t orbital charge lie within the sphere passing through the first shell of ions beyond the defect ions.

In calculating the energy levels we need Δ, the difference in potential energy and kinetic energy between the configuration $v^{n-1}t^{m+1}$ and the configuration v^nt^m. This corresponds to A–B in the notation of Coulson and Kearsley (1957), although here Δ depends on n. Thus Δ' refers to the $(vt^3)(v^2t^2)$ energy difference and Δ'' to the $(t^4)(vt^3)$ difference. Δ can be derived directly from the expressions (3) and the values of θ and ν; values of Δ are given in table 2 in the GF limit. From this table it can be seen that ν, θ and Δ vary relatively little with configuration. The mean value of Δ satisfies the Ivey law (see Gourary and Adrian 1960), $\Delta \sim 16\cdot82\, R^{-1\cdot54}$ ev, where R is in Å. Experimentally the corresponding relation for F-band energies is $E_{\mathrm{F}} \sim 17\cdot63\, R^{-1\cdot84}$ ev (Gourary and Adrian 1960). For diamond Δ agrees with Coulson and Kearsley's LCAO estimates which are 6·714 ev (unmodified) and 9·770 ev (modified calculation). Finally, it should be mentioned that if $1/\delta$ is increased from zero, with $\gamma = 0$, the fractional change in Δ is of order $2/(5\delta^2+1)$ and is less than 2% for $1/\delta$ as large as 0·2. This change in Δ includes the implicit dependence of ν and θ on δ. The neglect of the anisotropic terms in the potential can be justified by estimating their corrections to Δ in first-order perturbation theory. In the GF limit the terms up to the sixth-order cubic harmonic change Δ by less than 20%, representing a rather complete cancellation between the fourth- and sixth-order terms.

Table 2. The values of Δ, Δ' and Δ'' in ev

Crystal	Δ' (ev)	Δ'' (ev)	Δ (ev)
Diamond	8·602	8·764	8·683
LiF	6·944	7·790	7·367
KCl	3·975	4·254	4·115

Δ' is a $(vt^3)-(v^2t^2)$ energy difference, and Δ'' a $(t^4)-(vt^3)$ energy difference; $\Delta = \frac{1}{2}(\Delta'+\Delta'')$.

4. The calculation of electron–electron interaction integrals

The energy levels may be expressed in terms of Δ and a number of electron–electron interaction integrals of the general form

$$\langle pqrs\rangle = \iint d\mathbf{r}_1\, d\mathbf{r}_2\, p^*(\mathbf{r}_1)\, r(\mathbf{r}_1)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\, q^*(\mathbf{r}_2)\, s(\mathbf{r}_2)$$

in which p, q, r, s are normalized wave functions. The seven integrals of this type are

$$\begin{aligned} G &\equiv J_{0000} \equiv \langle vvvv\rangle, & G &\equiv J_{0011} \equiv \langle vvt_zt_z\rangle \\ D &\equiv J_{1111} \equiv \langle t_zt_zt_zt_z\rangle, & J &\equiv J_{1122} \equiv \langle t_xt_xt_zt_z\rangle \\ E &\equiv J_{0101} \equiv \langle vt_zvt_z\rangle, & K &\equiv -J_{0123} \equiv \langle vt_xt_yt_z\rangle \\ F &\equiv J_{1212} \equiv \langle t_zt_xt_zt_x\rangle, \end{aligned} \tag{4}$$

where the notations of both Coulson and Kearsley (1957) and of Yamaguchi (1962) are given for convenience. In the GF limit the K integral vanishes from parity considerations.

As one-centre wave functions are used these integrals can be calculated analytically in exactly the same way as such integrals are found for atoms (Condon and Shortley 1951). The angular parts of the wave functions are first broken down into sums of spherical harmonics and the integrals split into a sum of products of radial integrals and tabulated angular integrals. The radial integrals are of the form

$$R_k(pqrs) = \int_0^\infty dx\,\frac{P^*(x)R(x)}{x^{k-1}}\int_0^x dy\, Q^*(y)S(y)y^{k+2} + \int_0^\infty dx\, P^*(x)R(x)\,x^{k+2}\int_x^\infty dy\,\frac{Q^*(y)S(y)}{y^{k-1}}$$

where P, Q, R and S are the radial parts of p, q, r, s respectively. In the GF limit $\gamma = 1/\delta = 0$ we have

$$\begin{aligned} C &= R_0 & G &= \tfrac{1}{3}R_1 \\ D &= R_0+\tfrac{1}{25}R_2 & J &= \tfrac{3}{25}R_2 \\ E &= R_0 & K &= 0 \\ F &= R_0-\tfrac{2}{25}R_2 \end{aligned} \tag{5}$$

in which the R_k must be calculated using the radial functions appropriate to the integral involved. The corresponding expressions for arbitrary γ, δ are given in the appendix. With the exponential radial functions (2) P^*R and Q^*S are of the form $\exp(-\beta' r/R)$, $\exp(-\beta'' r/R)$ respectively. The R_k are particularly simple if $\beta' = \beta'' = \beta$, i.e. for $C\,(\beta = 2\nu)$, for $G\,(\beta = \theta + \nu)$ and for D, F and J $(\beta = 2\theta)$. Table 3 gives the R_k in these cases. For comparison we note that for delta-function radial functions $(|R'(r)|^2 \sim \delta(r-b))$, in which all the charge is at $r = b = \beta^+ R/2$, all the R_k are equal to $8{\cdot}309\beta^+/R$ ev. The two remaining cases where $\beta' \neq \beta''$ cases (E and K) are more complicated. Here we use the results of table 3 with $2\beta = \beta' + \beta''$, but multiply the R_k by a factor $\Phi_k(\beta'/\beta'')$. Although straightforward to calculate, the Φ_k are complicated in form and will not be given in full. For the E integral β'/β'' is ν/θ, or roughly 2; $\Phi_0\,(2)$ is 0·8691 (0·6667 for delta-function radial functions), $\Phi_1\,(2)$ is 0·7901 and $\Phi_2\,(2)$ is 0·7538. Φ_0 alone is needed in the GF limit, and for general x

Table 3. The radial integrals R_k in eV

$R_0 = 4{\cdot}4963\ \beta/R$
$R_1 = 2{\cdot}6978\ \beta/R$
$R_2 = 6{\cdot}8210\ \beta/R$
$R_3 = 7{\cdot}2972\ \beta/R$
$R_4 = 7{\cdot}8958\ \beta/R$
$R_5 = 8{\cdot}5648\ \beta/R$
$R_6 = 9{\cdot}3698\ \beta/R$

The radius R is in Å; β is a dimensionless parameter which is 2ν for C, 2θ for D, F and J, $\theta+\nu$ for G, $(\theta+\nu)\Phi_k(\nu/\theta)$ for E and $\tfrac{1}{2}(3\theta+\nu)\ \Phi_k\,\{\tfrac{1}{2}(1+\nu/\theta)\}$ for K.

$$\Phi_0(x) = \frac{16x}{5}\,\frac{1+3x+x^2}{(1+x)^4}.$$

The results of the calculations are given in table 4 for the GF limit; further values of the integrals are given in the appendix, and cover a wide range of γ and δ.

In this table, the LCAO calculations for diamond are those of Coulson and Kearsley (1957) and Yamaguchi (1962). The delta-function form of the radial functions may be more appropriate in this case where the atomic orbitals have relatively small overlap, as they concentrate the charge near the defect ions. The use of the delta-function form increases C, D, E and F by a factor of 1·9 and G by about 3. These changes lead to much better agreement between the one-centre and LCAO values. The J and K integrals remain much smaller in the one-centre results. This is not simply a result of using $\gamma = 1/\delta = 0$, for although both J and K can be increased by other choices of γ and δ they do not become as large as the LCAO values. Coulson and Kearsley's 'modified' values are closest to the one-centre results. Despite their small size these integrals are in fact critical in determining the ground state and the optical transition energy. Indeed the differences between the results of Coulson and Kearsley and those of Yamaguchi can be largely attributed to differences in their estimates of these integrals.

Table 4. Electron–electron interaction integrals in electron volts

	C	*D*	*E*	*F*	*G*	*J*	*K*
Diamond							
(*a*) One-centre	5·669	2·763	3·596	2·295	0·828	0·468	0
(*b*) LCAO							
Coulson & Kearsley							
(unmodified)	10·956	11·265	10·957	11·139	2·854	2·830	2·764
(modified)	10·207	9·307	9·865	8·954	1·700	0·759	1·217
Yamaguchi (case 1)	10·535	11·127	10·690	11·024	3·042	3·211	3·060
LiF							
(*a*) One-centre	7·371	3·488	4·634	2·897	1·066	0·591	0
(*b*) LCAO	5·330	5·926	5·107	3·939	1·204	0·365	0·508
KCl							
One-centre	5·666	3·057	3·716	2·539	0·855	0·518	0

The one-centre values here refer to the GF limit $\gamma = 1/\delta = 0$.

The LCAO results for LiF take for the atomic orbitals Li 2s orbitals centred on the defect ions. The various integrals can be calculated using the tables of Kotani *et al.* (1953). On the whole there is good agreement between LCAO and one-centre results. The K integral is again an exception, being larger in the LCAO case. By raising $1/\delta$ to the implausibly large value of 0·5 the two estimates become similar in magnitude.

In summary, the LCAO and one-centre calculations show reasonable agreement with the exception of the small integrals J and K, which are of importance in determining the ground state and transition energies.

5. The energy level structure

The secular equations which give the energy levels of the centre appear in table 2 of Yamaguchi (1962) and will not be reproduced here. The symmetry of the centre reduces these equations to three 3 × 3 secular determinants for ^1E, $^3T_1$ and $^1T_2$, a 2 × 2 determinant for $^1A_1$ and 1 × 1 determinants for the remaining states, $^1T_1$, $^3A_2$, ^3E, $^3T_2$ and $^5A_2$. In the GF limit $\gamma = 1/\delta = 0$ parity arguments show that the K integral vanishes, and the 3 × 3 determinants split into a 2 × 2 and a 1 × 1 determinant. Thus in this limit the largest secular determinant is 2 × 2. The low-lying energy levels are shown in figure 3.

5.1. *Diamond vacancy*

The predicted ground state is $^3T_1$, lying 0·468 ev below the ^1E state, which Coulson and Kearsley and Yamaguchi found as the ground state in the LCAO case. In the GF limit the sign of this energy difference does not depend on the form of the radial functions, as $E\,(^1E) = E\,(^3T_1) + \frac{1}{25}R_2$, where R_2 is always positive. The energy difference is, however, similar in size to G, J and K and is sensitive to changes in these integrals. The integrals in turn are sensitive to γ and δ, and for certain ranges of these the ^1E may be lowest. The largest effects come from the changes in K. Rather than investigate these in detail, we observe that the present one-centre approach is less appropriate to the vacancy in diamond than the LCAO approach, and it is unlikely to be reliable in predicting the order of two nearly degenerate states. The results of importance are that the ground state is not $^5A_2$, as predicted by Hund's rules, and that the two states lowest in energy (^1E and $^3T_1$) are nearly degenerate. Both the LCAO and one-centre approaches agree on these points. The actual order of the ^1E and $^3T_1$ states is further complicated by the fact that both these states should undergo Jahn–Teller distortions. In the GF limit the order of the energy levels, as shown in figure 3, is essentially the same as that of the $2s^n2p^{4-n}$ levels of the free carbon atom (Slater 1960, chap. 15). The conclusion that the ^1E and $^3T_1$ states are nearly degenerate may have some support from the spin resonance work of Owen (1965), who has observed a centre with a spin singlet ground state and a spin triplet excited state some 0·03 ev higher in energy. The centre may be a neutral vacancy or interstitial, possibly with a Jahn–Teller distortion.

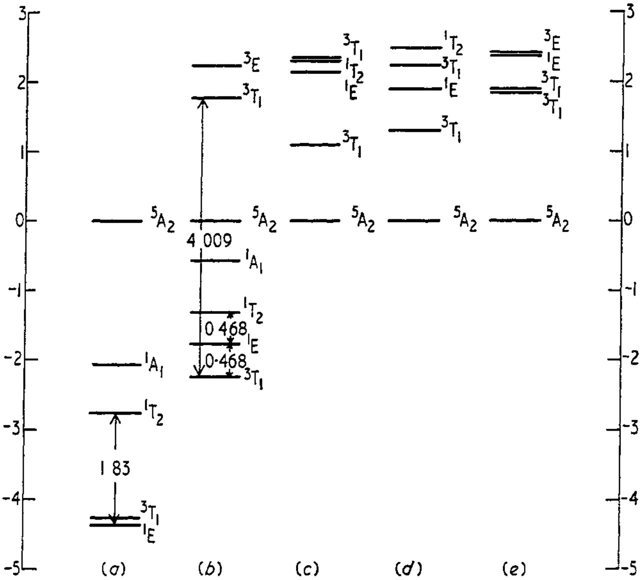

Figure 3. The calculated energy levels of the centre: (*a*) diamond vacancy (LCAO, Coulson and Kearsley's modified result, with their $P = -8{\cdot}18$ ev), (*b*) diamond vacancy (one-centre calculation), (*c*) N_2 centre in LiF (LCAO), (*d*) N_2 centre in LiF (one-centre calculation), (*e*) N_2 centre in KCl (one-centre calculation).

Coulson and Kearsley (1957) found that there was an allowed optical transition from their ^1E ground state, the energy of which was close to the 1·678 ev peak of the GR1 band (Clark *et al.* 1956), and concluded that the neutral vacancy was responsible for this band. This is contrary to the conclusion of Yamaguchi (1962) and is not consistent with the influence of stress on the band (Runciman 1965). The present calculations predict allowed transitions from the lowest two states which are $^3T_1 \leftrightarrow {}^3T_1$, with energy 4·01 ev, and $^1E \leftrightarrow {}^1T_2$, with energy 0·47 ev. There are no other allowed transitions of energy less than 5 ev. Although these energies vary with γ and δ, it does not seem possible to obtain energies near 2 ev, and it seems unlikely that the neutral vacancy is responsible for the GR1 band. This conclusion must be treated with some caution, for both the potential and the trial wave functions were chosen with the N_2 centre in mind. However, the potential only enters the problem directly in Δ, the value of which agrees well with the LCAO calculations. Further, the $^1E \leftrightarrow {}^1T_2$ transition energy does not seem very sensitive to the choice of wave function—the use of the delta-function radial functions, which concentrate the electronic charges at a given value of r, only changes this transition energy by about 20% from the value obtained above.

5.2. *LiF and KCl*

For these the predicted ground state is $^5A_2$ from both one-centre and LCAO calculations. The first excited state, $^3T_1$, is closer to the ground state in LiF than KCl. Comparing the results for the three systems, we see that as R is reduced from 2·619 Å for KCl to 1·741 Å for LiF and 1·5 Å for diamond the $^3T_1$ ground state becomes more probable. This can be understood from the discussion of § 2. The decrease in R raises both Δ and the electron–electron interaction integrals, although Δ increases more rapidly. At low R this favours the v^2t^2 configuration rather than the vt^3 configuration from which $^5A_2$ is derived.

The $^5A_2$ state should give rise to spin resonance. As the t electron wave functions extend over several unit cells the line may be broadened by hyperfine interactions. Of the states under consideration $^5A_2$ alone has spin 2; optical transitions from the $^5A_2$ state are therefore forbidden by the spin selection rule. It is thus unlikely that the N_2 band is caused by the N_2 centre in either KCl or LiF.

6. Conclusion

The energy levels of the tetrahedral N centre in KCl and LiF and of the neutral vacancy in diamond have been calculated. For diamond the ground state is not $^5A_2$, and the two lowest levels, ^1E and $^3T_1$, are nearly degenerate in energy. Neither of these states gives optical transitions, the energy of which is close to that of the GR1 band. For the N centres the ground state is $^5A_2$. This result contradicts the common view that aggregate F centres will have one optical absorption band of similar energy to the F band (Pick 1960), for the spin selection rule forbids transitions from the $^5A_2$ state. The tetrahedral N centre should be observable in spin resonance with spin 2.

Coulson and Kearsley (1957) and Yamaguchi (1962) considered the electronic structure of ionized centres in diamond. Two general conclusions can be drawn for ionized N centres of net charge $\pm e$. Firstly, whatever the ground state there is an allowed optical transition to some excited state derived from the same molecular orbitals. Secondly, the centre will have an odd number of electrons and will show spin resonance. Ionized centres have not been considered in the present article, as for the N centres the influence of lattice polarization on the energy levels raises important problems.

It is hoped to extend the present calculations to arbitrary R by adopting different radial functions for the even and odd parity terms in the wave functions, and ultimately by using Hartree–Fock wave functions.

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Appendix

We give here the values of the electron–electron interaction integrals for arbitrary γ, δ in terms of the R_k. For convenience we write $g = \gamma/\sqrt{210}$; then

$$C = R_0 + \frac{1{\cdot}7143g^2R_3 + 0{\cdot}3085g^4R_4 + 0{\cdot}1565g^4R_6}{(1+2g^2)^2}$$

$$D = R_0 + \frac{(0{\cdot}0816 + 0{\cdot}5714\delta^2 + \delta^4)R_2 + 1{\cdot}2245\delta^3R_3 + 0{\cdot}0816R_4}{(1+5\delta^2)^2}$$

$$E = R_0 + \frac{1{\cdot}1828\delta g R_3 + 0{\cdot}0808 g^2 R_4}{(1+5\delta^2)(1+2g^2)}$$

$$F = R_0 + \frac{(-0{\cdot}0408 + 0{\cdot}5714\delta^2 - 2\delta^4)R_2 + 0{\cdot}6122\delta^2 R_3 - 0{\cdot}0091 R_4}{(1+5\delta^2)^2}$$

$$G = \frac{(0{\cdot}2587g^2 + 2{\cdot}3920g\delta + 1{\cdot}6667\delta^2)R_1 + (0{\cdot}2000 + 0{\cdot}8280g\delta + 1{\cdot}200g^2\delta^2)R_2}{(1+5\delta^2)(1+2g^2)}$$
$$+ \frac{0{\cdot}1270g^2R_3 + 0{\cdot}6349g^2\delta^2R_4 + 0{\cdot}0892g^2R_5}{(1+5\delta^2)(1+2g^2)}$$

$$J = \frac{5\delta^2R_1 + (0{\cdot}0612 + 0{\cdot}8572\delta^2 + 3\delta^4)R_2 + 0{\cdot}7959\delta^2R_3 + 0{\cdot}0453R_4}{(1+5\delta^2)^2}$$

$$K = \frac{(1{\cdot}2910\delta^2 + 2{\cdot}4430g\delta)R_1 + (0{\cdot}1107 + 0{\cdot}7746\delta^2 + 0{\cdot}2469g\delta + 0{\cdot}5760g\delta^3)R_2}{(1+5\delta^2)^{3/2}(1+2g^2)^{1/2}}$$
$$+ \frac{0{\cdot}3292g\delta R_3 + 0{\cdot}1829g\delta R_4}{(1+5\delta^2)^{3/2}(1+2g^2)^{1/2}}.$$

Figure 4 shows the variation of these with g and δ for R_k obtained using the exponential radial functions of equation (2). The R_k are, of course, different for each integral—for example, C only involves v electrons and D only t electrons—and to convert the values in figure 2 to electron volts they must be multiplied by β/R Å, where β was defined in § 4. β is a function of ν and θ, and depends implicitly on g and δ.

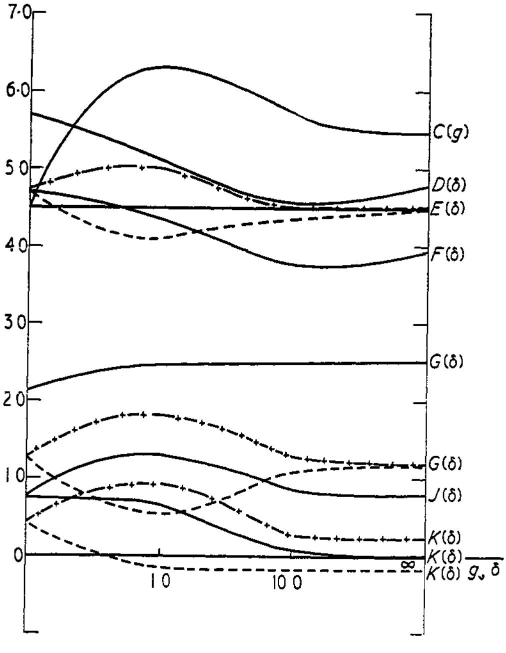

Figure 4. Schematic diagram of the electron–electron interaction integrals as functions of $g = \gamma/\sqrt{210}$ and δ. The curves shown are accurate for abscissae 0, 1, 10 and ∞. The integrals are in units of (β/R Å) ev. ——— $\delta = 0$ (C integral) or $g = 0$ (other integrals); – + – + $g = +1$; – – – – $g = -1$.

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