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## Two-electron defect systems in ionic crystals: application to $F'$ centres in alkali halides

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**Abstract.** The extended-ion method for the study of excited states in ionic crystals is modified for such two-electron defect systems as the  $F'$  centre and positronium in alkali halides. Exclusive use of 1s floating Gaussian functions as the basis is the main feature of the method. Some degree of electron correlation is built-in in this method. Applied to  $F'$  centres, it is found that in NaI the spin-singlet ground state is deeply bound, and there is also a bound triplet state. Comparison with experimental data regarding the optical and thermal dissociation energies in several alkali halides gives reasonable agreement.

### 1. Introduction

Previously, we have presented a hybrid potential method [1] for the study of one-electron defects in insulators based on the extended-ion approach. The method consists of two main features. First, the occupied core states are divided into two groups: the outmost s and p (OSP) shells, and the remaining deep core (DC). The DC part is represented by the first two orders ion-size parameters [2, 3], while the effects of the OSP are treated exactly. The second feature of this method is the exclusive use of 1s (floating) Gaussians. This allows the various terms (Coulomb, exchange and overlap) associated with the OSP electrons to be efficiently calculated. The method has since been successfully applied for the study of various defects, including self-trapped excitons in alkali halides [4] and in alkaline earth fluorides [5], as well as self-trapped exciton and impurity centres in rare gas solids [6]. In particular, calculations based on this method have predicted for the first time that the self-trapped excitons in alkali halides are generally off-centre [4].

The main purpose of this paper is to extend the hybrid potential method to treat a two-electron defect centre in an insulator such as the  $F'$  centre (with two electrons trapped at a single anion vacancy) in alkali halides. With certain modifications, the method can also be applied to the case of positrons and positronium trapped at defect centres in alkali halides. This will be studied in a subsequent paper [7]. Here we shall be only concerned with the  $F'$  centres in alkali halides.

In section 2, we present the general formalism. The defect wavefunction is represented as a linear combination of products of floating Gaussians, which are individually orthogonalized to the occupied core states. All the one-electron matrix elements can be treated in the same way as discussed in our earlier papers [1, 4, 6]. The most difficult term is the electron-electron interaction matrix element. In the appendix, we have shown that this can be approximated by simple interpolation formulae.

The lattice energy is treated in the usual way by means of the Born–Mayer type pair potential. For the polarization energy, the crystal is divided into two regions, the inner and outer regions. Ions in the inner region are relaxed explicitly by minimization of the system total energy, and the electronic polarization energy is calculated by the Mott–Littleton method [8]. The outer region is treated as a dielectric continuum.

We have applied the above method to study the  $F'$  centres in KCl, NaCl, NaBr and NaI. The results are presented and discussed in section 3. There have been several different methods employed to treat the  $F'$  centres in alkali halides. These include the continuum method [10], the polaron method [11], the point-ion model [12], and the extended-ion model [13]. A detailed discussion of earlier works is given in [14]. Among these, the point-ion model of La and Bartram [12] and the extended-ion model of Strozier and Dick [13] gave comparatively better results. Our method is most similar to that of the latter authors. We have calculated the optical binding energies and the thermal ionization energies for the  $F'$  centres. The results are in satisfactory agreement with available experimental data. We have also performed a study of the excited states. The results show that a bound excited singlet state can exist in NaI but marginally so in NaBr, which appears to be in agreement with experiment. Recently, various *ab initio* Hartree–Fock methods have become available for studies of defects [15]. These are ultimately the most desirable approaches of defect calculation. In order to keep the size of the quantum cluster reasonably small, various treatments are devised, such as the use of pseudopotentials and classical treatment of the region outside the quantum cluster. The task is quite complex, however. When the defect is excited, thereby occupying a diffuse state as in the excited F centre, the limited size of the quantum cluster becomes serious. Because of the different treatments proposed to various aspects, a direct comparison of *ab initio* methods and an approximate one like the present one is outside the scope of this work. A recent review [15] presents a useful overview of various methods currently in use.

## 2. Method of calculation

### 2.1. Electronic energy

To be definite, we consider the case of an  $F'$  centre in an alkali halide crystal. The method can readily be applied or adapted to treat other types of two-electron defects in insulators, such as positrons or positroniums in alkali halides. The electronic Hamiltonian of the  $F'$  centre has the form,

$$H = H_1 + H_2 + H_{12}. \quad (1)$$

Here

$$H_{12} = \frac{e^2}{|r_1 - r_2|} \quad (2)$$

is the Coulomb interaction between the two electrons at position  $r_1$  and  $r_2$ , and

$$H_i = -\frac{1}{2} \frac{\hbar^2}{m} \nabla_i^2 + V_{PI}(r_i) + [V(r_i) - V_{PI}(r_i)] \quad i = 1, 2 \dots \quad (3)$$

is the one-electron Hamiltonian.  $V_{PI}$  is the long range point-ion potential, and  $(V - V_{PI})$  represents the short range Coulomb and exchange interactions which can generally be represented as a sum of the contributions from each of the atoms at lattice sites  $\{R_\lambda\}$ .

The two-electron wavefunction of the  $F'$  centre is taken as a linear combination of a basis set of product functions,

$$\Phi(\mathbf{r}_1, \mathbf{r}_2) = \sum_k C_k \phi_{k,1}(\mathbf{r}_1) \phi_{k,2}(\mathbf{r}_2) \quad (4)$$

where the  $\phi$ s are 1s Gaussians, which are individually orthogonalized to the occupied core states  $\{\chi_{\gamma,\lambda}\}$ ,

$$\phi_{k,i}(\mathbf{r}_i) = G_{k,i}(\mathbf{r}_i) - \sum_{\gamma,\lambda} \langle \chi_{\gamma,\lambda} | G_{k,i} \rangle \chi_{\gamma,\lambda}(\mathbf{r}_i) \quad i = 1, 2, \dots \quad (5)$$

Here,

$$G_{k,i}(\mathbf{r}_i) = N_{k,i} \exp[-\alpha_{k,i} |\mathbf{r}_i - \xi_{k,i}|^2] \quad (6)$$

represents a normalized floating 1s Gaussian centred at  $\xi_{k,i}$ , which will also be denoted by  $G(\alpha_{k,i}, \xi_{k,i}; \mathbf{r}_i)$ . In the present work, the occupied cores of cations are represented by the free ion wavefunctions compiled by Clementi and Roetti [16]. While the cation wavefunctions are hardly modified in an ionic lattice, the anion orbitals undergo a considerable shrinking due to the attractive Madelung potential well. As in our earlier works [1, 4, 5], anion wavefunctions have been recalculated with an approximate point-ion lattice potential imposed in self-consistent field Hartree-Fock calculations. The use of untreated free anion orbitals leads to higher  $F$  centre absorption energy, among other things [1].

The electronic energy of the defect is determined by solving the secular equation

$$|H_{kl} - ES_{kl}| = 0 \quad (7)$$

where

$$S_{kl} = \langle \phi_{k,1} \phi_{k,2} | \phi_{l,1} \phi_{l,2} \rangle = \langle \phi_{k,1} | \phi_{l,1} \rangle \langle \phi_{k,2} | \phi_{l,2} \rangle \quad (8)$$

$$\begin{aligned} H_{k,l} = & \langle \phi_{k,1} \phi_{k,2} | H | \phi_{l,1} \phi_{l,2} \rangle = \langle \phi_{k,2} | \phi_{l,2} \rangle \langle \phi_{k,1} | H_1 | \phi_{l,1} \rangle \\ & + \langle \phi_{k,1} | \phi_{l,1} \rangle \langle \phi_{k,2} | H_2 | \phi_{l,2} \rangle + \langle \phi_{k,1} \phi_{k,2} | H_{12} | \phi_{l,1} \phi_{l,2} \rangle \end{aligned} \quad (9)$$

The overlaps  $\langle \phi_{k,i} | \phi_{l,i} \rangle$  and the one-electron matrix elements  $\langle \phi_{k,i} | H_i | \phi_{l,i} \rangle$  can be efficiently evaluated using the hybrid potential method described in earlier publications [1, 4, 6]. The most difficult term is the electron-electron interaction matrix element  $(H_{12})_{kl}$ , this being the last term in equation (9). The treatment of this new term represents a major effort of this work. Following the same principle as in the case of the one-electron matrix elements, we have attempted to fit  $(H_{12})_{kl}$  by some simple interpolation formula. The details and the interpolation forms are presented in the appendix. The method is very efficient, and in many respects can be regarded as an improvement over those of Wood and Wilson [17] and Strozier and Dick [13].

We note that the type of wavefunction in equation (4), which takes the form of a sum of product functions, has been employed in the early study of the hydrogen molecule. As discussed in details by Slater [18], this type of wavefunction takes explicit account of the effect of correlation. As an example, we consider the following form of basis:

$$\Phi = G(\alpha, \xi; \mathbf{r}_1) G(\alpha, -\xi; \mathbf{r}_2) + G(\alpha, -\xi; \mathbf{r}_1) G(\alpha, \xi; \mathbf{r}_2) \quad (10)$$

where the  $G$ s are 1s Gaussians as defined earlier.

It is straightforward to show that this can be rewritten as

$$(\exp[-2\alpha|\mathbf{R} - \boldsymbol{\xi}|^2] + \exp[-2\alpha|\mathbf{R} + \boldsymbol{\xi}|^2]) \exp[-(\alpha/2)|\mathbf{r}|^2] \quad (11)$$

Here,  $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$  and  $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ .

The explicit dependence on  $\mathbf{r}$  indicates that the wavefunction  $\Phi$  has taken account of some of the effects of correlation.

In the basis functions of equation (4), the spin part is not explicitly shown. Since the Hamiltonian  $H$  is symmetric with regard to the interchange ( $P_{12}$ ) of  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , eigenfunctions of  $H$  must be either (space) symmetric or antisymmetric with regard to  $P_{12}$ . These correspond, according to the Pauli's exclusion principle, to spin-singlet and spin-triplet states respectively. Thus, for the wavefunction in equation (4), it is crucial to include in the basis set  $\{\phi_{k,1}(\mathbf{r}_1)\phi_{k,2}(\mathbf{r}_2)\}$  the partners  $P_{12}[\phi_{k,1}(\mathbf{r}_1)\phi_{k,2}(\mathbf{r}_2)] (= \phi_{k,2}(\mathbf{r}_1)\phi_{k,1}(\mathbf{r}_2))$ . It is also necessary to include all the other partners required by symmetry. Then, diagonalization of  $H$  would yield directly symmetric (singlet) and antisymmetric (triplet) states of various symmetry. For example, the four basis functions  $\{G(\alpha, \mathbf{0}; \mathbf{r}_1)G(\alpha, \pm\boldsymbol{\xi}; \mathbf{r}_2), G(\alpha, \pm\boldsymbol{\xi}; \mathbf{r}_1)G(\alpha, \mathbf{0}; \mathbf{r}_2)\}$  with  $\boldsymbol{\xi} = (0, 0, d)$  would yield two singlet states and part of two triplet states.

## 2.2. Lattice and polarization energies

The lattice energy ( $E_{\text{lat}}$ ) consists of two parts, the lattice Coulomb energy and the short range repulsive energy. The Coulomb energy is the electrostatic energy of an infinite lattice of point ions. The repulsive energy is evaluated using the usual Born-Mayer potential  $V = A \exp(-r/\rho)$ . The values of the parameters  $A$  and  $\rho$  are calculated by the method of Reitz, Seitz and Genberg [19].

Since the  $F'$  centre is a defect with a net charge, the polarization effect is quite significant and also of long range. In this work, the lattice is divided into two regions: the inner region I containing ions close to the defect and the remaining outer region II. Ions in region I are relaxed explicitly to minimize the total energy of the system. The electronic polarization energy for this region is calculated by the lowest order Mott-Littleton method giving

$$E_{\text{pol}}^{(\text{I})} = -\frac{1}{2} \sum_{\gamma}^{(\text{I})} \boldsymbol{\mu}_{\gamma} \cdot \mathbf{E}_{\gamma} \quad (12)$$

Here,  $\mathbf{E}_{\gamma}$  is the electric field at the site of the ion due to the defect electrons and the point-ion lattice.  $\boldsymbol{\mu}_{\gamma}$  is the induced dipole which also reflects the interaction with other dipoles [20].  $\boldsymbol{\mu}$  has to be determined in a consistent way in equation (12), by iteration for example. We note that ionic polarization energy in this region has been accounted for by the lattice relaxation energy.

The outer region II is treated as a dielectric continuum following the method developed by Hardy and Lidiard [21]. The total (electronic and ionic) polarization energy has the form

$$E_{\text{pol}}^{(\text{II})} = \frac{1}{2} \int_{(\text{II})} \mathbf{E} \cdot \boldsymbol{\mu}(\mathbf{r}) \, d^3r \quad (13)$$

where  $\mathbf{E}$  is the local electric field, and  $\boldsymbol{\mu}$  is the total induced dipole per unit volume. Various parameters required in equation (13), such as the polarizabilities and the Szegedi charges, can be found in [22].

### 2.3. Method of minimization

The total energy of the defect system

$$E_{\text{tot}} = E_{\text{electron}} + E_{\text{lattice}} + E_{\text{pol}}^{(\text{I})} + E_{\text{pol}}^{(\text{II})} \quad (14)$$

is now to be minimized simultaneously with regard to the Gaussian exponents, the positions of the Gaussian basis function and the positions of the ions in region (I). In practice, it is generally sufficient to search first for the optimal wavefunction and then to determine the equilibrium lattice positions. Details of the method have been presented earlier [1, 4, 6]. It is also necessary to test the convergence of the total system energy with regard to the size of region (I).

## 3. Application to F' centres

We have applied the above method to study the ground and excited states of the F' centres in KCl, NaCl, NaBr and NaI. In the following we present and discuss the results of our calculations.

### 3.1. Lattice distortions

We first consider the ground state of the system which is a  $(1s)^2$  singlet. The simplest (pseudo) wavefunction has the form

$$\Phi_G(r_1, r_2) = G(\alpha, \mathbf{0}; r_1)G(\alpha, \mathbf{0}; r_2) \quad (15)$$

for which both electrons are centred on the vacancy site ( $\mathbf{0}$ ). As discussed above, we first determine the Gaussian exponent  $\alpha$  by minimization of the electronic energy with the lattice ions fixed at the perfect lattice configuration. Once  $\alpha$  is determined, the ions in region (I) are allowed to relax to minimize the total system energy in equation (14). Generally it is sufficient to include the four neighbouring shells to the vacancy as region (I). The results for the nearest-neighbour cation displacements are given in table 1. Experimental data are not available. Our results are generally larger than those of Berezin [23]; this may be partly due to the fact that in Berezin's work, only the first shell ions were allowed to relax. Our results also show quite substantial outward distortion for the second shell (about 5% of the cation-anion distance). The displacements of the third and fourth shell ions are generally small in comparison. Finally, we have used a larger basis set to improve the electronic energy at this relaxed lattice configuration. This basis consists of 5 bases of the form in equation (15) with  $\alpha = 0.03$ – $0.07$  a.u. and 6 bases of the form  $G(\alpha, \xi; r_1)G(\alpha, -\xi; r_2)$  as in equation (10). The electronic energy is lowered by about 0.7 eV. As discussed above, this is partly due to the effect of correlation. A large number of ions, about 300, contribute to  $E_{\text{electron}}$  through various short range potential energy terms.

We next consider the  $(1s2p)$  relaxed excited triplet state. First we note that a p-like wavefunction can be simulated by a pair of Gaussians,  $G(\alpha, \xi; r) - G(\alpha, -\xi; r)$ . Thus, the simplest wavefunction of the  $(1s2p_z)$  triplet state has the form

$$\begin{aligned} \Phi(r_1, r_2) = & G(\alpha, \mathbf{0}; r_1)[G(\alpha, \xi; r_2) - G(\alpha, -\xi; r_2)] \\ & - [G(\alpha, \xi; r_1) - G(\alpha, -\xi; r_1)]G(\alpha, \mathbf{0}; r_2) \end{aligned} \quad (16)$$

where  $\xi = (0, 0, \xi)$ . As with the ground state,  $\alpha$  and  $\xi$  are treated as variational parameters. Once these are determined, the lattice is relaxed to give the equilibrium ionic displacements. It is interesting to note that the two NN atoms on the  $z$ -axis have relatively smaller displacements. The total system energy is further minimized by enlarging the basis set. The final basis set consists of 3 bases of the form (16) with  $\alpha = 0.04, 0.05, 0.06$ .

**Table 1.** Calculated optical binding energy,  $E_{op}$  and thermal dissociation energy,  $E_{th}$ , of the  $F'$  centres are compared with experimental values (inside a bracket).  $E_g(F')$  and  $E_g(F)$  are the calculated ground state energy of the  $F'$  centre and F centre respectively in its own equilibrium lattice configuration.  $E_g(F^*)$  is the F centre energy in the distortion field of the  $F'$  centre ground state.  $\chi$  is the electron affinity.  $\Delta R_1$  is the first atomic shell relaxation of the  $F'$  centre ground state, given in Å. All energies are in eV.

	NaCl	KCl	NaBr	NaI
$E_g(F')$	3.75	4.33	3.21	0.31
$\Delta R_1$	0.33	0.45	0.53	0.79
$E_g(F)$	4.03	3.86	3.73	2.47
$E_g(F^*)$	5.98	5.61	6.05	4.64
$\chi$	0 <sup>a</sup>	0.41 <sup>b</sup>	(1.0)	1.5 <sup>a</sup>
			(assumed value)	
$E_{op}$	-2.23 (-1.72 <sup>c</sup> ) (-1.10 <sup>d</sup> )	-0.87 (-0.90 <sup>c</sup> ) (-1.00 <sup>e</sup> )	-1.84 (-1.55 <sup>f</sup> )	-2.83 (-1.90 <sup>f</sup> )
$E_{th}$	-0.28 (-0.5 <sup>g</sup> ) (-1.1 <sup>g</sup> )	0.88 (-0.40 <sup>h</sup> ) (-0.35 <sup>i</sup> )	0.48	-0.66 (-0.47 <sup>j</sup> ) (for KI)

<sup>a</sup> Reference [24].

<sup>b</sup> Reference [13].

<sup>c</sup> Reference [9].

<sup>d</sup> Reference [8b].

<sup>e</sup> Reference [27].

<sup>f</sup> Reference [28].

<sup>g</sup> Reference [29].

<sup>h</sup> Reference [30].

<sup>i</sup> Reference [31].

<sup>j</sup> Reference [32].

### 3.2. Optical binding energy

The optical binding energy of the  $F'$  centre,  $E_{op}(F')$ , is defined as the energy difference between the  $F'$  centre ground state and the photoionized  $F'$  centre state. However, in cluster calculations of this type, photoionized states are difficult to obtain. Alternatively, the binding energy can be written as

$$E_{op}(F') = (E_g(F^*) - \chi) - E_g(F') \quad (17)$$

where  $E_g(F')$  is the energy of the ground state of the  $F'$  centre,  $E_g(F^*)$  is the energy of the (unrelaxed) F centre ground state at the lattice configuration appropriate to the  $F'$  centre, and  $\chi$  is the binding energy of an electron at the bottom of the conduction band. Results of our calculations are presented in table 1. We have also included the thermal ionization energies which are calculated according to

$$E_{th}(F') = [E_g(F) - \chi] - E_g(F') \quad (18)$$

where  $E_g(F)$  is the energy of the relaxed ground state of the F centre. Our results are in satisfactory agreement with the experimental data for NaCl, as well as in general accord with an earlier calculation [13]. Similar experimental data for NaBr and NaI are not available. However, there is strong experimental evidence [26] that the ground state of the  $F'$  centre becomes more and more deeply bound from NaCl to NaI. This trend is indeed shown in the results of our calculation, table 1.

3.3. Excited states of  $F'$  centre in NaI

The results presented above show that the  $F'$  centre in KCl and NaCl has rather shallow binding energy which implies that the existence of a bound excited state is highly improbable. In fact we have found that the energy of the lowest  $1s2p$ -like excited state in NaCl is still greater than  $(E_g(F) - \chi)$ . Hence if formed, such states would spontaneously decay. On the other hand, the  $F'$  centres in NaBr and NaI are quite deeply bound, and there is experimental evidence that both NaBr and NaI have bound excited states [27]. The situation for NaI is of particular interest because of the unusual feature that its  $F'$  band has a Gaussian shape with narrow halfwidth (0.3 eV) and is located on the high energy side (2.4 eV) of the F band (2.1 eV), indicating the possible existence of a bound excited singlet state in this material. Absorption experiments have also suggested the existence of a bound triplet state [26]. Transitions from this state to the conduction band give rise to a broad band at 1.45 eV.

We have performed calculations for  $1s2p_z$ -like excited states of NaI using basis functions similar to equation (16) but of even parity. First, using the  $F'$  centre ground state distortion field, we have obtained the Franck-Condon transition energy to the  $(1s2p_z)$  excited singlet (ex.1) state:

$$\Delta E(g \rightarrow \text{ex.1}) = E_{\text{ex.1}}(F') - E_g(F') = 2.0 \text{ eV} \quad (19)$$

which is in reasonable agreement with experiment. For the relaxed excited triplet (ex.3) state, we first employed a minimal basis and determined the lattice configuration by minimization with regard to the lattice ion positions. A larger basis set is used to obtain a better estimate of the energy of the system,  $E_{\text{ex.3}}(F')$ . The same distortion field is then used to calculate the energy of the F centre,  $E_{\text{ex.3}}(F^*)$ , in the ionized state of the  $F'$  centre. The transition energy from the excited triplet state to the conduction band is given by:

$$\Delta E(\text{ex.3} \rightarrow \text{cond}) = [E_{\text{ex.3}}(F^*) - \chi] - E_{\text{ex.3}}(F') = 3.73 - 1.5 - 0.93 = 1.3 \text{ eV.} \quad (20)$$

which should be compared to the experimental value of 1.45 eV mentioned above. These data are assembled in table 2, together with those for NaBr.

**Table 2.** Calculated optical transition energies of the  $F'$  centre in NaI and NaBr. Experimental values are inside the bracket. All energies in eV.  $E_{\text{ex.1}}(F')$  and  $E_{\text{ex.3}}(F')$  stand respectively for the excited singlet and excited triplet  $F'$  centre states.  $E_{\text{ex.3}}(F^*)$  is for the F centres in the field of the triplet  $F'$  centres.

	NaBr	NaI
$E_g(F')$	3.21	0.31
$E_{\text{ex.1}}(F')$	5.49	2.28
$E_g \rightarrow E_{\text{ex.1}}$	-2.28	-1.97
		(-2.4 <sup>a</sup> )
$E_{\text{ex.3}}(F')$	4.35	0.93
$E_{\text{ex.3}}(F^*)$	5.31	3.73
$E_{\text{ex.3}} \rightarrow \text{ionization}$	0.04	-1.30
		(-1.45 <sup>a</sup> )

<sup>a</sup> Reference [23].

The case for NaBr is somewhat intermediate between NaCl and NaI. We have also found that the bound excited triplet state may exist in this material. It is interesting to note



in this regard that in the case of the  $H^-$  ion, being an hydrogen analogue of the  $F'$  centre, theoretical work has been unable to prove or disprove the existence of a bound triplet state.

In this paper we have presented an efficient method of calculating the structure of two-electron defect systems in alkali halides within the approximation of the extended ion method. It is based on a systematic use of spherically symmetric floating Gaussian functions as bases. The results obtained for the  $F'$  centre in several alkali halides are in reasonable accord with observed data. In NaI, we found deeply bound  $F'$  centre ground state, as well as possibly bound triplet state. The deeply bound  $F'$  centre raises the question of possible negative  $U$  effect in NaI. The present method, after some modifications, is applied to the study of free and self-trapped positronium in alkali halides [7].

### Appendix. The electron-electron interaction integral

Upon substitution of equation (5) into  $(H_{12})_{kl}$ , the last term in equation (9), we find that  $(H_{12})_{kl}$  can be written as a sum of terms which can be classified into five categories:  $0\chi$ ,  $1\chi$ ,  $2\chi$ ,  $3\chi$ , and  $4\chi$  terms. Here an  $n\chi$  term ( $n = 0-4$ ) represents an integral of  $H_{12}$  involving  $n$  core orbitals  $\chi_{\gamma,\lambda}$  and  $(4-n)$  Gaussians, multiplied by  $n$  overlaps  $\langle X_{\gamma,\gamma} | G_{ki} \rangle$ . We further classify the  $2\chi$  terms as  $2\chi$  Coulomb-like terms or  $2\chi$  exchange-like terms according to whether the two core orbitals in the integral have the same or different electronic coordinates.

There is only one  $0\chi$  term, which involves four Gaussians, and this represents the dominant contribution to  $(H_{12})_{kl}$ . All the other terms involve overlaps between the Gaussians and the occupied core states. For localized defects, such as the  $F'$  centre, the overlap with the DC orbitals is much smaller than that with OSP orbitals. Thus we shall only be concerned with the OSP orbitals in all the  $n\chi$  terms.

Initially all these terms are accurately evaluated after the OSP orbitals are represented by a large number ( $\sim 15$ ) of Gaussians. The results of this tedious calculation show that only the  $1\chi$  and  $2\chi$  Coulomb-like terms are dominant because the other terms are at least two orders of magnitude smaller.

To further reduce the computing time, we have attempted to represent the outer s, p orbitals by single normalized Gaussians:

$$\begin{aligned} \chi_s &\rightarrow A_s N_s \exp[-\beta_s r^2] \\ \chi_{pz} &\rightarrow A_p N_p z \exp[-\beta_p r^2] \end{aligned}$$

where the parameters  $A$  and  $\beta$  are adjusted so as to fit the exact values of the  $1\chi$  and  $2\chi$  Coulomb-like terms. The fitting was performed by the least squares method.

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