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A study of the self-trapped and free positronium states in alkali halide crystals

C G Zhang and K S Song

Department of Physics, University of Ottawa, Ottawa, Ontario, K1N 6N5, Canada

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Abstract. A theoretical study of the positronium state in alkali halide crystals is presented using the extended-ion approach adapted for two-particle systems. For both the electron and the positron, floating $1s$ Gaussian functions were used as the basis. The energies of the Bloch-like free state at $k = 0$ and of a self-trapped positronium state localized at an interstitial site were calculated. Lattice relaxation and polarization were included in the self-trapped state. It is found that both the free and self-trapped states have very close energies, separated by less than 0.2 eV, and the self-trapped state has a quite extended wavefunction. The calculated angular correlation curve of two γ annihilations is in fair agreement with the experimental result for KCl. The calculated two-photon decay lifetime is longer than the experimental value by about an order of magnitude, and it is attributed to the Gaussian basis functions that are used. In the angular correlation curve of the free positronium state, a series of weak satellite peaks that reflect the periodic symmetry of the Bloch state were observed experimentally, i.e. in KI and NaI, with some of the peaks vanishingly small (crystallographic effect). This effect is beautifully reproduced in this work. It can be interpreted to be due to the positronium being unable to distinguish the cations from the anions, and as a result the NaCl structure is seen as a simple-cubic structure by the free positronium.

1. Introduction

The study of the positronium (Ps) in alkali halides has a history of more than 30 years. In 1956 Ferrell [1] predicted that the bound pair of a positron and an electron would not be stable in the perfect alkali halide crystals. The experiment at room temperature of Stewart and Pope [2], in which no narrow peak (Ps peak) was observed in the angular correlation curves (ACC) of alkali chlorides and sodium halides, seemed to support this argument. Later, Bisi *et al* [3, 4] measured positron lifetime spectra for some alkali halides and obtained results that suggested the formation of a Ps or Ps-like state in the specimen. On the other hand, Herlach [5] showed by comparing the data with and without a magnetic field that a narrow component was in fact contained in the apparently smooth ACC of KCl. Following this observation, Dannefaer and Smedskjaer [6, 7] made multiple-component parameter fittings to the ACC of NaCl and KCl and were able to correlate their narrowest component with the decay of the singlet Ps.

In the early 1970s [8–12], a great deal of experimental work was conducted to study positron annihilation in alkali halides with substantial concentrations of F centres. The significant change in the angular distribution of two-photon annihilation was found and attributed to annihilation of positrons trapped by F centres. Positron annihilation associated with various types of vacancies was studied actively during that period of time.

The research in this area has been enhanced after Hyodo and Takakusa [13] discovered that Ps does exist in a delocalized state in NaF and NaCl at low temperatures. The evidence

for delocalized Ps was provided by angular correlation measurements with very narrow peaks in the momentum distribution of the annihilation photon pair at sufficiently low temperature; such narrowness results only when the wavefunction of the Ps is extended over the crystal as a Bloch wave. Similar studies have shown that delocalized Ps is formed also in several other alkali halides such as KBr [13], KI [14], NaI [14], RbCl [15] and KCl [16]. It has been shown that above a characteristic temperature the narrow para-Ps peak in the angular correlation curve broadens drastically. This broadening was interpreted as indicating the localization of Ps in a metastable, self-trapped state [17]. Therefore the Ps atom may reside in either a delocalized or a localized state, with the energy level of the localized state assumed to lie higher than the bottom of the delocalized Bloch band. At low temperature, Ps will be mainly in the delocalized state but will, with rising temperature, start to populate the localized states. This effect has been attributed to a temperature-induced transition of the Ps to a self-trapped state.

Generally speaking, the progress in experimental research in this area has been quite impressive, well ahead of theoretical studies. There have been very few theoretical works involving detailed calculation on Bloch-state Ps and metastable self-trapped Ps. We have adapted an earlier successful version of the extended-ion method, based on the use of floating Gaussian orbitals (FGO) as the basis functions [18], to study the defect systems with two electrons such as the F^{\prime} centres in alkali halides [19] (this paper is referred to as I hereafter). For systems involving a positron and an electron, certain modifications to the method discussed in I have been made. The two-particle system is described by a linear combination of product functions, each part representing one particle. The single-particle basis is made exclusively of FGO in which the Gaussian damping constant as well as the position are varied. As we noted in I, this type of basis incorporates some degree of electron-positron correlation from the start. The electron-positron correlation is an essential character of the systems being studied in this work. The use of an FGO basis allows an efficient evaluation of various terms in the single-particle Hartree-Fock equation. However, as will be discussed below, the relative and the centre-of-mass (CM) parts of the Ps wavefunction are not independently optimized in the variational solution of the problem.

In this paper we present the work on several Ps-related systems in NaF, NaCl and KCl at 0 K and room temperature. Using a method specially adapted for Ps from that used in I, we have studied the structure of the Bloch-like free Ps and the self-trapped Ps state centred on an interstitial site and compared their energies. We found that their energies are rather close, in qualitative agreement with the report of Hyodo *et al* [17]. We have also calculated the lifetimes and angular correlation curves (ACC) of two-photon decay of the Ps. The calculated lifetimes are found to be about one order of magnitude larger than those obtained experimentally for both delocalized and localized Ps. We attribute this to the particular form of the Gaussian basis that we have chosen to use.

The ACC calculated in this work are compared with those obtained experimentally for the self-trapped Ps. We found good agreement with experimental data when the centre-of-mass (CM) motion was allowed to spread out over many unit cells by means of an envelope function (which was determined from energy minimization). A basis localized on a single interstitial site gave a broad ACC in poor agreement with the experiment, and also resulted in a strong lattice relaxation. Regarding the ACC of the free Ps, Kasai and Fujiwara [14] have found an interesting crystallographic effect in KI and NaI. The satellite peaks corresponding to $p_z = nh/a$ (a is the lattice constant and n are odd integers) are vanishingly small compared with those for even n . The Ps behaves as if the NaCl lattice were reduced to one of simple-cubic structure with half the original lattice constant. This effect is analogous to the disappearing diffraction peaks in the x-ray diffraction in KCl

[20]. We have obtained a very good account of this effect in NaF, NaCl and KCl in this study. Our study confirms the interpretation given by Kasai and Fujiwara. We have also obtained reasonable results for the intensity ratio of the first satellite peak ($p_z = 2h/a$) to the central peak. The Ps trapped at an anion vacancy (Fe^+ centre) is also studied, which yielded reasonable lifetimes and ACC.

This paper is organized as follows. In section 2, we describe the method, referring to I for the common parts. In section 3, the results of the self-trapped and free Ps states are given in detail. A brief account for the Fe^+ centre follows.

2. Method of calculation

Basically, the defect systems under study are composed of two particles. In the approach we have developed, the two-particle basis functions are represented by a product of two single-particle floating Gaussian orbitals.

As mentioned before, we are going to study several distinct systems in this work. Obviously, they have quite different electronic structures from one another, and hence their Hartree-Fock Hamiltonians will be described separately.

2.1. Electronic energy calculation

2.1.1. Bloch-like positronium state. Here we propose a way to calculate the Bloch state of the Ps. It turns out that the approach with floating 1s Gaussian basis has a significant potential even in an energy band calculation [21].

Since the interaction of a correlated Ps with a periodic lattice is invariant under translation by a lattice vector, the total crystal momentum of the Ps is a good quantum number to label the eigenstates of the system and the corresponding energy eigenvalues.

We formulate a Bloch function for the Ps that satisfies the Bloch theorem:

$$\psi(\mathbf{r}_+ + \mathbf{d}, \mathbf{r}_- + \mathbf{d}) = e^{i\mathbf{k}\cdot\mathbf{d}}\psi(\mathbf{r}_+, \mathbf{r}_-) \quad (1)$$

for an arbitrary lattice vector \mathbf{d} . Here, \mathbf{r}_+ and \mathbf{r}_- represent the positions of positron and electron respectively. Thus the wavefunction can be constructed from the Bloch sum of the following form:

$$\begin{aligned} \psi(\mathbf{r}_+, \mathbf{r}_-) = & \frac{1}{\sqrt{N}} \sum_i C_i \sum_L e^{i\mathbf{k}\cdot\mathbf{L}} \left(G_i(\mathbf{r}_- - \mathbf{L}) - \sum_{m,\lambda} \langle \chi_{\lambda,m}(\mathbf{r}_-) | G_i(\mathbf{r}_-) \rangle \chi_{\lambda,L+m}(\mathbf{r}_-) \right) \\ & \times G(\mathbf{r}_+ - \mathbf{L}) \end{aligned} \quad (2)$$

where N is the number of unit cells, G_i the floating Gaussian, \mathbf{k} the Bloch-state positronium wavevector, \mathbf{L} the atomic site, and $\chi_{\lambda,m}(\mathbf{r}_-)$ a core orbital λ centred at m . The floating spherically symmetric Gaussian basis has been described in I, and some of the important properties are shown in the appendix. Summation over \mathbf{L} runs over all unit cells. We note that the electron part has been explicitly orthogonalized to occupied core states as in I, but the positron part has not. It can be shown that equation (2) satisfies the Bloch theorem.

We are interested in the behaviour of the delocalized Ps state at the centre of the Brillouin zone, so the wavevector \mathbf{k} can be simply taken to be zero. Hereafter $G_i^+ \equiv G_i(\mathbf{r}_+)$. The Bloch wavefunction (2) yields the Hamiltonian matrix element, which can be written as

$$H_{ij} = H_{ij}^- + H_{ij}^+ + H_{ij}^{+-} \quad (3)$$

where the first term is a standard single-electron Hamiltonian, the second term represents a single-positron Hamiltonian, which has similar form to the first one except for the missing exchange interaction, and the third represents the interaction between the two particles. More explicitly, they are

$$H^- = -\frac{1}{2}\nabla_-^2 + V_{\text{pi}}(r_-) + V_{\text{sc}}(r_-) + V_{\text{ex}}(r_-) \quad (3a)$$

$$H^+ = -\frac{1}{2}\nabla_+^2 - V_{\text{pi}}(r_+) - V_{\text{sc}}(r_+) \quad (3b)$$

$$H^{+-} = -e^2/|r_+ - r_-|. \quad (3c)$$

The first term of (3) has the following explicit expression:

$$\begin{aligned} H_{ij}^- &= \sum_L \langle G_i^- | H^- | G_j^- (L) \rangle \langle G_i^+ | G_j^+ (L) \rangle \\ &\quad - \sum_{m,L,\lambda} \varepsilon_{\lambda,m+L} \langle G_i^- | \chi_{\lambda,m+L} \rangle \langle \chi_{\lambda,m} | G_j^- \rangle \langle G_i^+ | G_j^+ (L) \rangle \\ &\quad - \sum_{m,L,\lambda} \varepsilon_{\lambda,m} \langle G_i^- | \chi_{\lambda,m} \rangle \langle \chi_{\lambda,m} | G_j^- (L) \rangle \langle G_i^+ | G_j^+ (L) \rangle \\ &\quad + \sum_{\lambda,\lambda',L,m,m'} \varepsilon_{\lambda',m'} \langle G_i^- | \chi_{\lambda',m'} \rangle \langle \chi_{\lambda,m} | G_j^- \rangle \langle \chi_{\lambda',m'} | \chi_{\lambda,m+L} \rangle \langle G_i^+ | G_j^+ (L) \rangle. \end{aligned} \quad (4)$$

Here $\varepsilon_{\lambda,m}$ is the core energy. As a result of the translational symmetry, one of the summations over L cancels $1/N$. The orthogonality of different core orbitals reduces the multiple summations in the last term of (4), and cancels the second term. Then equation (4) simplifies to

$$\begin{aligned} H_{ij}^- &= \sum_L \langle G_i^- | H^- | G_j^- (L) \rangle \langle G_i^+ | G_j^+ (L) \rangle \\ &\quad - \sum_{m,L,\lambda} \varepsilon_{\lambda,m} \langle G_i^- | \chi_{\lambda,m} \rangle \langle \chi_{\lambda,m} | G_j^- (L) \rangle \langle G_i^+ | G_j^+ (L) \rangle. \end{aligned} \quad (5)$$

Following the same procedure, we have the matrix element for the positron Hamiltonian:

$$\begin{aligned} H_{ij}^+ &= \sum_L \langle G_i^- | G_j^- (L) \rangle \langle G_i^+ | H^+ | G_j^+ (L) \rangle \\ &\quad - \sum_{L,\lambda,m} \langle G_i^- | \chi_{\lambda,m} \rangle \langle \chi_{\lambda,m} | G_j^- (L) \rangle \langle G_i^+ | H^+ | G_j^+ (L) \rangle. \end{aligned} \quad (6)$$

The matrix element of the interaction Hamiltonian has a complicated form:

$$\begin{aligned} H_{ij}^{+-} &= \sum_L \langle G_i^+ G_i^- | H^{+-} | G_j^+ (L) G_j^- (L) \rangle - \sum_{L,\lambda,m} \langle \chi_{\lambda,m} | G_j^- \rangle \langle G_i^- G_i^+ | H^{+-} | \chi_{\lambda,m+L} G_j^+ (L) \rangle \\ &\quad - \sum_{L,\lambda,m} \langle G_i^- | \chi_{\lambda,m} \rangle \langle G_i^+ \chi_{\lambda,m} | H^{+-} | G_j^+ (L) G_j^- (L) \rangle \\ &\quad + \sum_{L,\lambda,\lambda',m,m'} \langle G_i^- | \chi_{\lambda',m'} \rangle \langle \chi_{\lambda,m} | G_j^- \rangle \langle G_i^+ \chi_{\lambda',m'} | H^{+-} | G_j^+ (L) \chi_{\lambda,m+L} \rangle. \end{aligned} \quad (7)$$

The overlap matrix element is

$$S_{ij} = \sum_{\mathbf{L}} \langle G_i^- | G_j^- (\mathbf{L}) \rangle \langle G_i^+ | G_j^+ (\mathbf{L}) \rangle - \sum_{\mathbf{L}, \lambda, m} \langle G_i^- | \chi_{\lambda, m} \rangle \langle \chi_{\lambda, m} | G_j^- (\mathbf{L}) \rangle \langle G_i^+ | G_j^+ (\mathbf{L}) \rangle. \quad (8)$$

We have derived the general expressions for various matrix elements. The details of the calculation of the above equation are given in I, in our study of the F' centres.

The most complicated terms are seen in (7), which represent the electron-positron interaction. Because the positron wavefunction has not been orthogonalized, there is considerable simplification compared to the F' centre, described in I. The various terms involving H^{+-} are evaluated as explained in I.

The calculation of the total overlap matrix element (8) is much simpler. The energies and the eigenfunctions are obtained by solving the secular determinant

$$|H_{ij} - ES_{ij}| = 0. \quad (9)$$

In a non-relativistic approach, the energy levels are degenerate with regard to the spin and angular momentum states. In the Russell-Saunders coupling, each Russell-Saunders eigenstate is an eigenstate of the charge conjugation operator, belonging to the eigenvalue $(-1)^{l+s}$. For a spherically symmetric state ($l = 0$), then we have singlet state $(-1)^{s=0}$ and triplet state $(-1)^{s=1}$. As our Hamiltonian does not contain the spin explicitly, we do not need to give spin explicitly in our wavefunction. The diagonalization of the Hamiltonian results in symmetrized space wavefunctions, which take care of the singlet and triplet space states automatically. The space symmetric state corresponds to the spin singlet state and the space antisymmetric state to the spin triplet state.

2.1.2. The self-trapped positronium state. As mentioned in the introduction, Ps could be self-trapped at an interstitial site in a perfect crystal above a certain temperature. There is a lattice relaxation around the trapped site that stabilizes the system.

In a preliminary study, we first studied a strongly localized system. It resulted in a fairly tight system with a substantial lattice expansion ($\sim 16\%$ and 8% for cation and anion of the first neighbour atom of NaCl). This also gave an ACC that was found to be too broadly distributed compared to the experimental data [16]. We interpreted this to be related to the type of basis function we used. The product of two Gaussians, one for each particle, can be transformed such that the coordinates of the CM and the coordinates of the relative motion of the two particles are explicitly shown (appendix). The difficulty with this type of basis is that it is not possible to have variational freedom for both the CM and relative motion of the Ps at the same time. We concluded that, as the relative motion is optimized, there must be a separate control over the CM part.

Now we describe this approach in detail. The idea is similar to that which describes the exciton wave packet with an envelope function [22], and the wavefunction of the system can be written as

$$\psi(\mathbf{r}_+, \mathbf{r}_-) = \sum_i C_i \sum_{\mathbf{R}} \exp(-\alpha_R R^2) \phi_i(\mathbf{r}_+ - \mathbf{R}) \phi_i(\mathbf{r}_- - \mathbf{R}). \quad (10)$$

Here \mathbf{R} represents the position of the unit cell, and the summation over \mathbf{R} runs over all unit cells. As we can see, a Gaussian envelope function is proposed. In other words, the envelope function allows the CM of the Ps to spread over like a wave packet and the decay parameter is determined through energy minimization.

Finally the Hamiltonian matrix element for this system can be expressed as

$$\begin{aligned}
 H_{ij} &= \left\langle \sum_{\mathbf{R}} F(\mathbf{R}) \phi_i(\mathbf{r}_+ - \mathbf{R}) \phi_i(\mathbf{r}_- - \mathbf{R}) \middle| H \middle| \sum_{\mathbf{R}'} F(\mathbf{R}') \phi_j(\mathbf{r}_+ - \mathbf{R}') \phi_j(\mathbf{r}_- - \mathbf{R}') \right\rangle \\
 &= \sum_{\mathbf{R}, \mathbf{R}'} F(\mathbf{R}') \bar{F}(\mathbf{R}) \langle \phi_i(\mathbf{r}_+ - \mathbf{R}) \phi_i(\mathbf{r}_- - \mathbf{R}) | H | \phi_j(\mathbf{r}_+ - \mathbf{R}') \phi_j(\mathbf{r}_- - \mathbf{R}') \rangle.
 \end{aligned}
 \tag{11}$$

The total overlap matrix element is

$$S_{ij} = \sum_{\mathbf{R}, \mathbf{R}'} F(\mathbf{R}') F(\mathbf{R}) \langle \phi_i(\mathbf{r}_+ - \mathbf{R}) \phi_i(\mathbf{r}_- - \mathbf{R}) | \phi_j(\mathbf{r}_+ - \mathbf{R}') \phi_j(\mathbf{r}_- - \mathbf{R}') \rangle.
 \tag{12}$$

The Gaussian-type envelope function represents no further difficulty in calculation.

2.1.3. Fe^+ centre. For this system, the defect is composed of an anion vacancy plus an electron–positron pair. We investigated this system by following the above procedure. The wavefunction can be simply taken from equation (2) with $L = 0$. The Hamiltonian follows from equations (3)–(7), except that there is a missing anion in the point-ion potential.

2.2. Lattice energy

The lattice energy includes the Coulomb energy between point ions, short-range repulsive energy and polarization energy. It is known that an intrinsic Ps state exhibits a temperature effect. We have considered the self-trapped and free Ps states at 0 K and room temperature (300 K) by refitting the Born–Mayer pair potential to these temperatures.

Polarization effects depend very much on the defect charge. Its calculation is subject to various approximations. In our approach, we adopt the Mott–Littleton method to estimate the polarization effect. Systems such as the Ps self-trapped at an interstice are charge-neutral defects, and the polarization effects turn out to be quite small. Their calculations are therefore similar to that of an F centre while the charged defect of Fe^+ centre is treated in the same way as the F' centre. For details refer to I.

The Bloch-like state of the Ps behaves in a slightly different way because of the translational symmetry. Polarization effects are to be treated also based on the lowest-order Mott–Littleton method.

2.3. Lifetime calculation

Information on the behaviour of the positron in solids is transmitted exclusively by the annihilation radiation. The expression of the lifetime τ is given by

$$\Gamma = \frac{1}{\tau} = \pi \alpha^3 \int \psi^*(\mathbf{r}_-, \mathbf{r}_+) \delta(\mathbf{r}_- - \mathbf{r}_+) \psi(\mathbf{r}_-, \mathbf{r}_+) d\mathbf{r}_- d\mathbf{r}_+.
 \tag{13}$$

Here α is the fine-structure constant. Depending on the wavefunctions of the various systems studied, it yields the lifetime. Taking the example of a localized Ps state, it becomes

$$\Gamma = \frac{1}{\tau} = \pi \alpha^3 \sum_{i,j} C_i C_j \int \left(G_i^- - \sum_{\lambda,m} \langle G_i^- | \chi_{\lambda,m} \rangle \chi_{\lambda,m} \right)$$

$$\begin{aligned}
& \times G_i^+ \left(G_j^- - \sum_{\lambda', m'} \langle \chi_{\lambda', m'} | G_j^- \rangle \chi_{\lambda', m'} \right) G_j^+ dr \\
= & \pi \alpha^3 \sum_{i, j} C_i C_j \left(\langle G_i^- G_i^+ | G_j^- G_j^+ \rangle - \sum_{\lambda, m} \langle G_i^- | \chi_{\lambda, m} \rangle \langle \chi_{\lambda, m} G_i^+ | G_j^- G_j^+ \rangle \right. \\
& - \sum_{\lambda', m'} \langle \chi_{\lambda', m'} | G_j^- \rangle \langle G_i^- G_i^+ | \chi_{\lambda', m'} G_j^+ \rangle \\
& \left. + \sum_{\lambda', m'} \langle \chi_{\lambda', m'} | G_j^- \rangle \langle G_i^- | \chi_{\lambda, m} \rangle \langle \chi_{\lambda, m} G_i^+ | \chi_{\lambda', m'} G_j^+ \rangle \right). \quad (14)
\end{aligned}$$

The first term on the right represents the zeroth-order approximation to the rate and its calculation is straightforward. The remaining terms represent the corrections from consideration of the core effects. We assume that the compact deep core orbitals are less important than outer *s* and *p* shells in lifetime, and thereby we avoid treating complicated deep core contributions. We tried an indirect way to see the impact of deep cores on the lifetime. The outer *s* and *p* shells are fitted into Gaussians in our approach. The interpolated decay parameters of the Gaussians were made 10 times larger, or, in other words, the diffuse outer shells were made artificially compact, so that they behave somewhat like deep cores. The lifetime was recalculated by using such 'deep cores' and it was found that the lifetime varied by about 1%. Therefore, we decided to drop the contributions of the deep cores in (14). The second and the third terms are relatively simple, because the three Gaussians can be contracted into a single Gaussian and χ are either *s* orbital or *p* orbitals. The interpolation scheme is applied here to calculate the ion-size correction on the lifetime. The last term involves two cores, which can be at different sites. We assume those interpolation formulae are still valid and replace the cores by fitted Gaussians. We need to work out all configurations regarding the different orbitals and then sum them up. Generally, this term is smaller, and as the distance between the two cores increases it decreases fast. For Ps in the Bloch state we consider only the floating Gaussian part in the wavefunction to calculate the rate approximately, which means all influences on lifetime from core orbitals are ignored.

2.4. Angular correlation calculation

The angular distribution of two-photon annihilation $N(\theta)$ is the experimentally measured quantity. Here, θ is a small angle (of the order of milliradian) and represents the angular deviation of the two γ quanta from 180° . The deviation from 180° represents the effect of linear momentum that the Ps has at the time of self-annihilation. We first have to calculate the momentum density $P(\mathbf{p})$ of the Ps:

$$P(\mathbf{p}) = \left| \int e^{i\mathbf{p}\cdot\mathbf{r}} \delta(\mathbf{r}_- - \mathbf{r}_+) \psi(\mathbf{r}_-, \mathbf{r}_+) d\mathbf{r}_- d\mathbf{r}_+ \right|^2 = \left| \int e^{i\mathbf{p}\cdot\mathbf{r}} \psi(\mathbf{r}, \mathbf{r}) d\mathbf{r} \right|^2 = |a(\mathbf{p})|^2 \quad (15)$$

where $a(\mathbf{p})$ is the Fourier transform of the wavefunction $\psi(\mathbf{r}, \mathbf{r})$. The one-dimensional angular momentum correlation is defined as (in atomic units):

$$N(\theta) = \int P(P_x, P_y, P_z = \theta/\alpha) dp_x dp_y \quad (16)$$

where $p_z = c\theta = \theta/\alpha$ and $\alpha = 1/c$ is the fine-structure constant. For localized-state Ps and Bloch-state Ps, neglecting the contribution of the core orbitals through orthogonalization, the evaluation of (16) involves only the floating Gaussians and is straightforward.

3. Results and discussion

In this section, we present results and discussions for each of the systems separately.

3.1. The Bloch-like positronium state

Previously in section 2.1.1, we have described how to represent the delocalized Bloch-like Ps state. We have studied two main aspects of the Bloch-like Ps state. One is the relative stability of the delocalized state compared with that of the localized self-trapped state to be presented in section 3.2. This is done by evaluating the Bloch-like Ps state energy at the bottom of the Ps band, $k = 0$, at two temperatures, 0 and 300 K. The other is the so-called crystallographic effect observed by Kasai and Fujiwara [14] in the satellite peaks of the ACC. The self-annihilation of Ps from a Bloch state is identified by a series of narrow peaks appearing on the ACC, the positions of which correspond to the projections of the reciprocal lattice vectors onto the scanning direction. Kasai and Fujiwara have noted that the peaks corresponding to the reciprocal lattice points of odd indices are anomalously weak, as reproduced in figure 1. This implies that the Ps atom is moving in the crystal without distinguishing the anion from the cation, and therefore experiences the periodicity of a simple-cubic lattice of lattice constant $a/2$ rather than a face-centred-cubic lattice of lattice constant a .

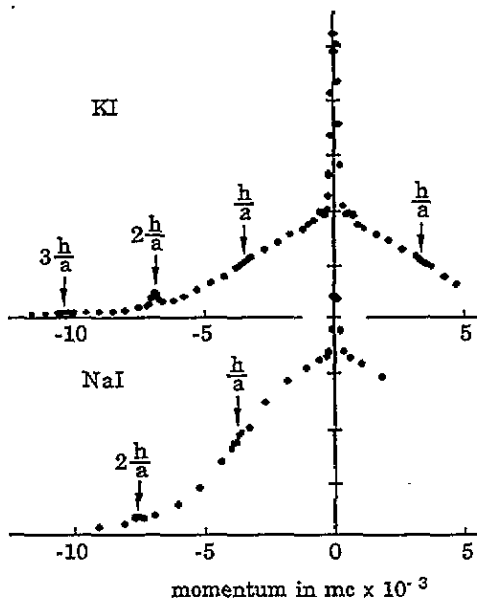


Figure 1. The angular correlation of two gamma rays from positrons annihilating in single crystals of KI and NaI oriented nearly along the (1,0,0) direction. Note the anomalously weak intensities of the first satellite peaks. Resolution: $0.178mc \times 10^{-3}$. Horizontal axis represents momentum in $mc \times 10^{-3}$. The figure is from Kasai and Fujiwara [14], reproduced with permission.

3.1.1. Energy of the free positronium state. There are two interstitial sites in one unit cell, i.e. $(1/2, 1/2, 1/2)$ and $(1/2, 1/2, -1/2)$ in units of anion-cation distance. If we place the basis only at one of them, we are assuming that the Ps atoms can distinguish the anion and cation, and experience the periodicity of an FCC lattice. If we want to examine the crystallographic effect, we have to adopt the hypothesis proposed by Kasai and Fujiwara [14], and consider the other equivalent site of the unit cell also. The pair basis (PB) has to be employed, with equivalent basis placed on the two sites just described. Our use of the

floating Gaussian basis makes this very convenient. One pair of the on-centre basis (that is to say, both particles are centred on the interstitial site) is used and the calculated energies are presented in table 1. It is interesting to note that the energies evaluated with the pair basis are slightly lower than those with the single basis (SB). Energy calculation of a Bloch state involves lattice sums, as shown in equation (7), and takes a considerable amount of computer time. For this reason, a maximum of two Bloch bases was used throughout. For a meaningful comparison of relative energy difference between the free and self-trapped Ps states, we also employed a similar quality basis in our study of the self-trapped state. The energies of free and self-trapped states are compared below in section 3.2.1.

Table 1. Calculated lowest energy levels (at both 0 and 300 K) and lifetimes (at 0 K) of the delocalized-state Ps. E_{Bloch} represents the Bloch-state Ps energy. SB and PB are abbreviations of single basis and pair basis. τ and τ_{exp} represent the calculated and experimental lifetimes.

	NaF	NaCl	KCl	T (K)
$E_{\text{Bloch}}(\text{SB})$ (eV)	8.77	2.43	0.97	300
$E_{\text{Bloch}}(\text{PB})$ (eV)	7.64	2.30	0.91	300
$E_{\text{Bloch}}(\text{SB})$ (eV)	8.95	2.61	1.09	0
$E_{\text{Bloch}}(\text{PB})$ (eV)	8.03	2.47	1.04	0
τ (ns)	0.95	1.64	1.80	0
τ_{exp} (ns)	0.083 [23]		0.087 [23]	0

3.1.2. Positronium lifetime and angular correlation. The lifetimes evaluated from our model (presented in table 1) are more than 10 times larger than the observed values. Our lifetime calculation is generally unsatisfactory and it is believed to be related to the form of the basis functions used. A detailed discussion on this matter will be given in section 3.2.2, together with the case of the self-trapped Ps. In terms of the angular correlation, what can be observed from Bloch-state Ps are the central peak and a few satellite peaks corresponding to the projections of reciprocal lattice vectors onto the scanning directions. For one-dimensional angular correlation, the projection of an arbitrary reciprocal lattice vector g on the z direction, g_z , determines the positions of those peaks; $g_z = 0, \pm 1, \pm 2, \dots, (2\pi/a)$ correspond to the central peak, first satellite, second satellite, and so on. Actually, they reflect the periodicity of the lattice. To examine the interesting crystallographic effect, we can demonstrate this effect through our calculation of angular correlation. We use the PB to calculate those peaks.

It is seen from table 2 that, when the PB are used, the satellite peaks corresponding to odd-index g_z are dramatically reduced to practically zero. It implies that the Ps atoms seem not to see the difference between the anion and cation, and move like they are in the simple-cubic lattice with half the period of the original FCC lattice. This is the first theoretical proof of the observed crystallographic effect.

In Kasai and Fujiwara's experiment [14], they also reported the ratio between the central peak and the first satellite peak of reciprocal lattice vector of the simple-cubic lattice for KI being 15/1 (see figure 1). Our calculated ratios for NaF, NaCl and KCl are 14.4/1, 12.3/1 and 8.6/1, respectively. As can be seen, they fit observations quite well.

3.2. The positronium self-trapped at an interstice

3.2.1. Lattice relaxation and ground-state energy. As we described in the method in section 2.1.2, the best result regarding the ACC was obtained when a flexible CM

Table 2. Calculated peak heights of the two gamma decay angular correlation curve (at 0 K) for the Bloch-state Ps. SB and PB are abbreviations for single basis and pair basis (see text for detail). g_z represents the projections of reciprocal lattice vector on z direction.

	$g_z(n2\pi/a) = 0$	1	2	3
NaF N (SB)	1.15	0.43	0.09	0.002
NaF N (PB)	2.02	0	0.14	0
NaCl N (SB)	1.17	0.45	0.09	0.001
NaCl N (PB)	2.09	0	0.17	0
KCl N (SB)	1.24	0.60	0.14	0.09
KCl N (PB)	2.32	0	0.27	0
KI (exp.)	1.00	≈ 0	0.067 [14]	≈ 0

wavefunction was devised. Without this device, the centre of mass of Ps turned out to be too restricted in space, leading to a much too broad ACC and substantial lattice relaxation. Therefore, we report here the result obtained with an envelope function that allows a separate variational degree of freedom to the CM.

The extended CM envelope function is multiplied by the localized Ps wavefunction and is summed over unit cells (see equation (10)). The envelope function is represented by a Gaussian function that is centred at the central unit cell and its decay parameter is determined through energy optimization. In our calculation, it comes out to be 0.01 au.

We also found that using a pair of Ps bases localized on two equivalent interstitial sites, $(1/2, 1/2, 1/2)$ and $(1/2, 1/2, -1/2)$ in units of anion-cation distance, gives lower energy by about 0.1 eV (in NaCl and KCl) and 0.9 eV (in NaF). Table 3 shows results obtained with this pair of localized bases modulated by the envelope function. The lattice relaxation is about 0.1 Å for the nearest-neighbour ions, and indicates an expansion.

Table 3. Calculated lowest energy levels (at both 0 and 300 K) and lifetimes (at 0 K) of the localized-state Ps. E_{loc} represents the localized-state Ps energy. SB and PB are abbreviations for single basis and pair basis. τ (no core), τ_c (with core) and τ_{exp} represent the calculated and experimental lifetimes.

	NaF	NaCl	KCl	T (K)
$E_{loc}(SB)$ (eV)	8.77	2.47	0.99	300
$E_{loc}(PB)$ (eV)	7.85	2.32	0.84	300
$E_{loc}(SB)$ (eV)	9.10	2.67	1.13	0
$E_{loc}(PB)$ (eV)	8.20	2.59	1.11	0
τ (ns)	1.40	1.81	2.23	0
τ_c (ns)	1.20	1.44	1.78	0
τ_{exp} (ns)	0.091 [23]		0.106 [23]	0

3.2.2. Positronium lifetime and angular correlation. Hyodo and Stewart [23] proposed a model to deduce lifetimes of KCl and NaF for both localized and delocalized Ps based on their observations. Though there are some arguments on this model [24], we present their values for localized Ps in table 3. For both the free and self-trapped Ps, our calculated lifetimes are quite large compared to the experimental data (tables 1 and 3). As described in section 2.3, the lifetime is a quantity that depends on the value of wavefunction at $r_+ = r_-$ (zero of relative distance). The exponential function that describes correctly the relative motion of Ps has a cusp at $r = 0$, while a Gaussian does not. The behaviour of the relative coordinate wavefunction at the origin is an important factor in determining the lifetime [25].

Although the product of two single-particle Gaussians can be rewritten so that the CM and relative coordinates can be made explicit, as shown in the appendix, the two parts cannot be variationally optimized in an independent way. Using a large basis set can improve this situation. Because of the increasing computing time, the size of the basis set has been restricted to two for both the free and self-trapped Ps. As a result, the relative motion of the Ps is not fully optimized, contributing possibly to the poor lifetimes obtained.

ACC are calculated by using the envelope-modulated wavefunction of equation (10). The ACC of KCl calculated are shown in figure 2 together with the experimental data obtained by Kasai and Hyodo [16]. We are only interested in the Ps self-annihilation, so the observed ACC in figure 2 is the Ps momentum distribution in KCl obtained by subtracting the broad component. There is a fairly good agreement between the two, which indicates that the self-trapped Ps has a fairly diffuse distribution as can be seen from the envelope Gaussian function with $\alpha_R = 0.01$ (in atomic units).

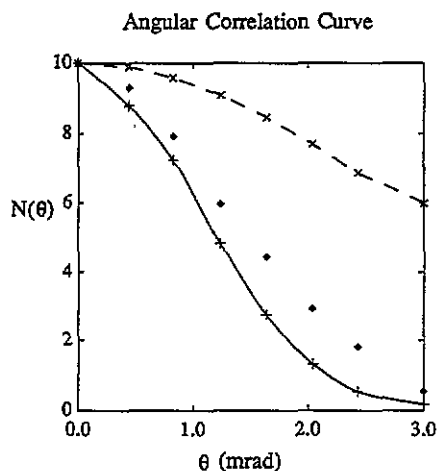


Figure 2. Angular correlation curves of localized Ps at an interstice in KCl. Squares are experimental data from Kasai *et al* [16]. The broken curve is the theoretical calculation based on the non-envelope-modulated wavefunction, and the full curve is the theoretical calculation by using the envelope-modulated wavefunction. Curves are normalized such that $N(\theta) = 10$ at $\theta = 0$.

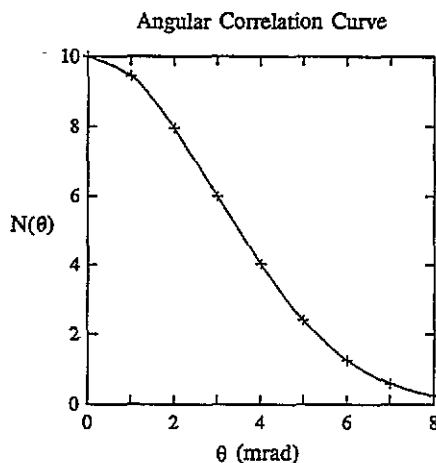


Figure 3. Angular correlation curve $N(\theta)$ for two-photon annihilation from F centres in NaF. The curve shows the theoretical result using the large basis set (see the text for details). Normalization of $N(\theta)$ is made such that $N(\theta) = 10$ at $\theta = 0$.

The parameter L , which was chosen as the quantity to measure the spatial extension of the CM of the self-trapped Ps, has been estimated by several authors before. Assuming that the Ps pair is represented by a Gaussian wave packet, its Fourier transform and angular momentum distribution can be derived. Through fitting the full width at half-maximum (FWHM) of the momentum distribution, $W_{1/2}$, with observed data, the L value can be estimated [16, 17] as $L(\text{\AA}) = 10.7 \times 10^{-3} mc / W_{1/2}$, where m is the mass of an electron and c the speed of light. Hyodo, Kasai and Fujiwara [15, 17] measured angular correlation curves of NaF, KCl and some other alkali halides as well. Based on their experimental data and the above equation, they drew a conclusion from their estimation of L that the localization length is of the order of the nearest anion-cation distance. For NaF and KCl, they got the values 3.2 \AA and 3.5 \AA , respectively. With decay factor 0.01 au of the extension of the CM,

the calculated L turns out to be 3.7 Å, which fits well with those derived by Hyodo *et al* [15, 17].

In the model proposed by Hyodo *et al* [17], the Ps atom have two kinds of states, free and self-trapped, which are separated by an adiabatic potential barrier. They estimated the energy level of the self-trapped state to be about 0.1 eV above the bottom of the delocalized band [17]. It is seen from tables 1 and 3 that this energy difference is small (between 0.25 eV and zero). Because our calculation has an uncertainty of about 0.2 eV, we conclude that the energy level of self-trapped Ps state is very close to that of the Bloch Ps state. The present study is therefore in qualitative agreement with the experimental observations [16, 17]. We have not attempted to determine the existence of the potential barrier between the two types of Ps states. According to the fundamental theory of self-trapping of an exciton (and also positronium by analogy), the existence of a potential barrier between the free and self-trapped states is well understood in three-dimensional systems [26]. It is especially true because short-range interaction is dominant between exciton (and also positronium) and lattice.

3.3. Fe^+ centres

3.3.1. Lattice relaxation and binding energy. This system is formed by an F centre trapping a positron. Both electron and positron are well localized at the anion vacancy. The vacancy itself has the symmetry of point group O_h . It is found that the lowest ground-state energy is obtained when the Gaussian parameters α^- and α^+ are identical for the two particles. The lattice is relaxed using first a single optimized basis, centred at the vacancy. In the process of energy minimization, ions surrounding the defect are moving outwards without breaking the O_h symmetry. Up to the fourth-shell ions are relaxed.

The first nearest-neighbour ions are displaced (designated as D_{nn} hereafter) quite an amount due to the stronger polarization effect from the extra charge at the vacancy. After the lattice relaxation is determined, we added the off-centre basis (basis placed around the defect along the three crystal axes) to improve the electronic energy. We need to optimize both decay parameters and the positions of the off-centre basis. Altogether, 16 floating Gaussians are used (four of on-centre type and two sets of off-centre type).

Following previous workers, the binding energy of a positron to an F centre is defined as [25]

$$E_b = E(F^*) - E(Fe^+)$$

i.e. the energy difference between the ground-state F centre and an Fe^+ centre. $E(F^*)$ represents the F-centre ground-state energy calculated at the Fe^+ -centre ground-state lattice relaxation in accordance with the Franck–Condon principle, because the binding energy here is referred to optical excitation.

The binding energies of three crystals (table 4) are calculated using the large basis described above. A few conclusions can be drawn: (i) Positron binding energies to the F centre range from 1 to 2 eV for the alkali halides we studied, and, as the size of cation increases, binding gets deeper, which agrees generally with previous calculations. (ii) The binding mainly comes from electron–positron correlation. Adding two sets of off-centre bases lowers the ground-state energy by about 1 eV.

Positron binding energies to F centres were estimated before by Berezin [27] and Farazdel and Cade [25]. Berezin used the Hulthén potential to calculate the binding energies for a few alkali halides and those values he found were 1.4 eV for NaCl, 1.6 eV for KCl and 1.7 eV for KBr. The correlation was totally ignored in his calculation. Two

Table 4. Calculated Fe^+ -centre ground-state parameters (at 0 K). D_{nn} represents the nearest-neighbour ion displacements. E_t and E_b represent respectively the equilibrium energy and binding energy, calculated with the large basis (see the text). τ_0 and τ represent the lifetimes calculated with a single optimized on-centre basis and the large basis, respectively. τ_c refers to the lifetimes calculated with the core effect counted. τ_{exp} is the observed lifetimes.

	NaF	NaCl	KCl
D_{nn} (Å)	0.34	0.29	0.29
$E_t(\text{F}^*)$ (eV)	8.23	4.80	4.52
$E_t(\text{Fe}^+)$ (eV)	7.04	3.60	2.82
E_b (eV)	1.19	1.20	1.70
τ_0 (ns)	3.31	4.68	4.65
τ (ns)	1.90	2.55	2.59
τ_c (ns)	1.60	2.20	2.40
τ_{exp} (ns)		1.10 [16]	1.20 [16]

model potentials (hydrogenic potential and Krumhansl–Schwartz potential) were used by Farazdel and Cade, and three types of trial wavefunctions (uncorrelated, partly correlated and correlated) were applied to calculate the binding energies. Their binding energies vary considerably depending on the potential and trial wavefunction used. For both potentials the correlated wavefunction gave binding energies 1–2 eV larger than the uncorrelated wavefunction. The model potentials made a large difference. In terms of uncorrelated wavefunction, the hydrogenic potential led to quite deep binding energies, varying about 1–2 eV for different crystals, while the Krumhansl–Schwartz potential did not show strong sign of binding.

The binding energies calculated by our model agree with those obtained by both Farazdel and Berezin in the sense that their values are in about the same range as ours. As a matter of fact, our values are closer to what Farazdel *et al.* obtained by using the Krumhansl–Schwartz potential with correlated wavefunction. Berezin's treatment is relatively crude owing to the lack of correlation effect. On the other hand, none of the above work incorporated lattice relaxation explicitly; instead the lattice environment was represented by a model potential. So far there have been no experimental results reported for binding energy. Our work is the only one involving detailed lattice environment and both correlation effect and lattice relaxation effects can be estimated. In terms of electron description, our Gaussian wavefunction is not as good as the Slater wavefunction, but the linear combination of many Gaussians seems to make up for this shortcoming. The self-consistent treatment of defect and lattice provides information about the ionic relaxation around the defect simultaneously. Both Fe^+ centre and F centre are treated by exactly the same approach. The excited state of the Fe^+ centre is examined for (1s2p) configuration, i.e. the electron is in 1s ground state and the positron is in the excited p-like state. The calculation is tried only for NaCl and the energy obtained is 7.1 eV. The F-centre ground-state energy under the same lattice distortion comes out to be 5.12 eV (ionized state). Obviously the binding is impossible, or we can say the ground state is the only possible binding state for Fe^+ centres.

3.3.2. *Positronium lifetime and angular correlation.* Similar to the above energy calculation, the results are obtained for both the single on-centre basis and the large basis including two sets of off-centre Gaussians. We also want to examine the contributions from core electrons to the lifetime.

Our calculated lifetime values for NaCl and KCl are about twice as long as those observed. Comparing calculated lifetimes with core effect (τ_c) to the ones without core effect (τ_0 for single optimized basis and τ for large basis), we see that taking core orbitals

into account does not improve the lifetime appreciably. But introducing the off-centre type basis (shown as τ) does improve the lifetime significantly. When compared to the lifetimes of free and self-trapped Ps presented above, the relative agreement with observed data is better. This is probably due to the use of a very large basis in the present case as well as to the fact that Fe^+ is well localized on the anion vacancy.

Angular correlation curves (ACC) of Ps annihilation are one of the most frequently reported data. The calculated ACC for NaF, NaCl and KCl are drawn in figures 3, 4 and 5 respectively. The experimental measurements for NaCl and KCl [28] are also shown in the figures. A comparison for NaCl can be made with the similar graph in Farazdel's paper [25]. In figures 4 and 5, two calculated curves are displayed in each figure. One is calculated with the single on-centre basis, and the other with the large basis already described above. Generally, both agree with experiment fairly well. But the large basis improves the calculation very appreciably. Those figures clearly show the effect of better basis.

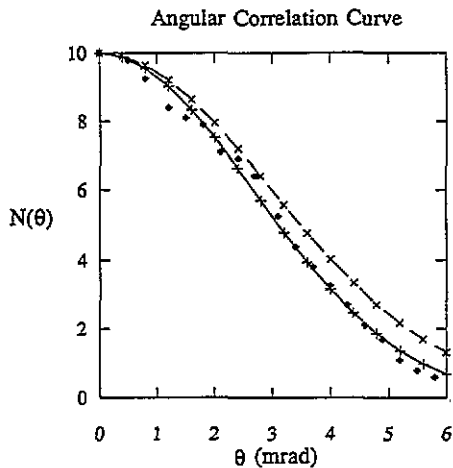


Figure 4. Angular correlation curves $N(\theta)$ for two-photon annihilation of positrons from F centres in NaCl. The full curve represents the theoretical calculation using the large basis set, and the broken curve is that using a single optimized on-centre basis. Squares are experimental data from Herlach and Oggenfuss [28]. Normalization of $N(\theta)$ is made such that $N(\theta) = 10$ at $\theta = 0$.

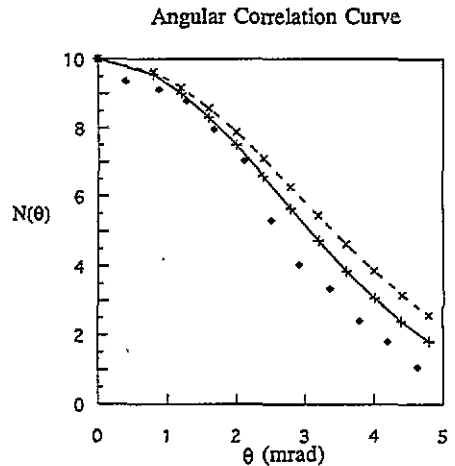


Figure 5. Angular correlation curves $N(\theta)$ for two-photon annihilation of positrons from F centres in KCl. The full curve represents the theoretical calculations using the large basis set and the broken curve is that using a single optimized on-centre basis. Squares are experimental data from Herlach and Oggenfuss [28]. Normalization of $N(\theta)$ is made such that $N(\theta) = 10$ at $\theta = 0$.

Now we examine the calculations made by Farazdel and Cade. Their figure of ACC shows that the best fit comes from the uncorrelated wavefunction with hydrogen potential. Even though the partly correlated and correlated wavefunctions give better energy and lifetime, the deviations for ACC are quite large. The improvements of energy and ACC go in opposite directions. It is not clear why this is so. Our calculation shows that the large basis yields better results not only for ACC but also for energy and lifetime.

It is believed that the centre-of-mass motion of the Ps pair has an energy distribution that follows the Boltzmann distribution: the distribution of momentum is proportional to $\exp(-p^2/2MkT)$. On the other hand, as our basis contains a centre of mass of Ps with a Gaussian wavefunction $\exp(-\alpha R^2)$, its Fourier transform results in a similar form. The use

of the Gaussian basis provides an unexpected advantage in representing the distribution of momentum p at thermal equilibrium. The best ACC for Fe^+ centre are obtained from our method.

4. Summary

In this work, we have studied the structure of several defects involving the positronium in alkali halide crystals. The systematic investigations resulted in overall features of various systems that are found to be in reasonable agreement with experiment, except the lifetimes in the cases of self-trapped and delocalized Bloch-like Ps states.

The advantage of our method is the ease with which it can be applied under the same approximations to many defect systems such as the F centre, Fe^+ centre, localized Ps and free Ps. Those positronium systems associated with a defect-free lattice have been found to be more interesting in both experiment and theory. We found both the free and self-trapped Ps to be very close in energy. The free state is a truly Bloch-like state and exhibits the crystallographic effect with missing peaks in the ACC. The self-trapped state is found to be fairly extended over many unit cells, as described by the envelope function we introduced.

All in all, we have developed a successful method along the lines of the extended-ion approach for dealing with those complicated defect systems possessing more than one 'electron'. Not only has a considerable amount of results associated with various positron or positronium systems been achieved, but several important features of observations are satisfactorily explained.

Acknowledgments

One of the authors (KSS) would like to express his thanks to Professor A T Stewart for drawing the author's interest to the problem of the Ps self-trapping.

Appendix

Basically, the defect systems under study are composed of two particles. In the approach we have developed, the two-particle basis is represented by a product wavefunction of two single-particle Gaussian basis functions. In the following, we present the relation between our basis and a more conventional basis in which the centre-of-mass and relative motions are explicitly described. We use an arbitrary two-particle product Gaussian basis of the form, centred at A and B (normalization constants are not considered):

$$\exp(-\alpha|r_1 - A|^2) \exp(-\beta|r_2 - B|^2). \quad (\text{A1})$$

We transform the coordinates into a CM coordinate system by defining

$$r = r_1 - r_2 \quad R = \frac{1}{2}(r_1 + r_2). \quad (\text{A2})$$

Then (A1) can be written as

$$\exp(-\alpha|\frac{1}{2}r + R - A|^2) \exp(-\beta|R - \frac{1}{2}r - B|^2) = G(R)G(r) \quad (\text{A3})$$

where

$$G(\mathbf{R}) = \exp\{-[\alpha\beta/(\alpha + \beta)]|2\mathbf{R} - \mathbf{A} - \mathbf{B}|^2\} \quad (\text{A4})$$

$$G(\mathbf{r}) = \exp\{-(\alpha + \beta)|\frac{1}{2}\mathbf{r} - [\alpha\mathbf{A} - \beta\mathbf{B} + (\beta - \alpha)\mathbf{R}]/(\alpha + \beta)|^2\}. \quad (\text{A5})$$

Here, one of the properties of Gaussian functions has been used, in which a product of two Gaussians can be contracted into a new Gaussian with a new decay factor and at a new position. The basis decouples partly into the product of CM and relative motions. This can be seen more transparently when the Gaussians have a common decay factor ($\alpha = \beta$), and their positions are chosen in such a way that $\mathbf{A} = \mathbf{B}$ or $\mathbf{A} = -\mathbf{B}$. Then (A3) becomes either of the following forms:

$$G(\mathbf{R})G(\mathbf{r}) = \exp(-2\alpha|\mathbf{R} - \mathbf{A}|^2) \exp(-\frac{1}{2}\alpha|\mathbf{r}|^2) \quad (\text{A6})$$

$$G(\mathbf{R})G(\mathbf{r}) = \exp(-2\alpha|\mathbf{R}|^2) \exp(-\frac{1}{2}\alpha|\mathbf{r} - 2\mathbf{A}|^2). \quad (\text{A7})$$

As was discussed in section 3.3 and in I, the basis we employ has some degree of built-in correlation effect between the two particles.

Note added in proof. Dr T Hyodo has pointed out to the author (KSS) that consideration of the 'pick off' process by the surrounding atoms could shorten the calculated lifetimes. We thank him for this remark.

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