

Ab initio calculations of the excitonic spectra of the alkali iodides including relativistic effects

Patrick W. Goalwin

Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

A. Barry Kunz

Physics Department, Michigan Technological University, Houghton, Michigan 49931

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We extend our previous studies of local excitons in the alkali halides to include relativistic effects such as spin-orbit, mass-velocity, and Darwin corrections. We examine the alkali iodide series and certain features in the optical absorption spectra which are due to local excitons. We find that we must include relativistic effects, as well as an appropriate number of neighboring-ion shells, if we are to compute the excitonic energies accurately.

INTRODUCTION

In this paper, we extend the studies of local excitons reported in a previous paper to include the alkali iodide series.¹

For the alkali iodide series we have included relativistic effects (I has $Z=53$) using a perturbation-theory method. The inclusion of relativistic effects is necessary, if we are to extend the methods used previously to systems involving heavy atoms in a quantitative way. We developed new computer codes to treat relativistic effects, using perturbation theory, as part of this study.

Optical-absorption studies have been carried out on alkali iodides in the ultraviolet region. It has been hypothesized that certain features in the experimental spectrum can be explained using excitons on the halide ion.² The excitons are believed to be of the Frenkel type, in which the excited state is localized on a single atomic site but the spectrum is complicated by the proximity of excited d states to the usual s states. In our previous paper we reported on excitons in the alkali chlorides.¹

The experimental results may be readily summarized. In LiI and NaI the most important features of the spectra are two low-lying peaks. In RbI, KI, and CsI there are four distinct low-lying peaks and a host of observed shoulders and smaller features. The same pattern is observed in the alkali bromides. In both cases, the separation of the lowest-lying peaks appears to increase for the materials with lighter and smaller alkali ions. A similar pattern is observed for the alkali bromides. However, for the chloride there are at most three peaks and the splitting of the two lowest peaks is invariant from material to material.

Phillips³ has discussed the splitting for both excitons and interband transitions in the alkali iodides. He finds that the splitting for both excitonic and interband transitions is about 0.3 eV greater in NaI than in KI and RbI. He is unable to explain this effect. Kunz⁴ looked at the

splitting for the interband transition and was able to show that the enhancement is due to overlap of the wave functions of the second-nearest-neighbor iodide ions. This overlap is much larger for LiI and NaI than it is for KI and RbI. Due to the very small size of the sodium and lithium ions relative to the iodide ion, this is to be expected. If one neglects the overlap of the iodide wave functions, one should expect less-accurate results for NaI and LiI than for KI and RbI.

There have been several previous efforts to study the effects of relativistic corrections in the alkali halides. Onodera and Okazaki⁵ developed a formalism for the relativistic-Green's-function calculations of the band structure and applied this formalism to KI and CsI. They used the Dirac equation in their work. Kunz⁶ made calculations of the band structure for LiI, NaI, KI, and RbI, including relativistic effects as perturbations. Kunz^{4,6} also computed spin-orbit parameters for all the alkali chlorides, bromides, and iodides using a band-structure technique, including proper treatment of overlap, and was able to account for the observed splittings. The work of Osaka *et al.*⁷ on the charge-transfer model exciton included a spin-orbit correction which used atomic spin-orbit parameters.

There has also been work done in the general area of computing relativistic corrections to Schrödinger's equation. Herman and Skillman⁸ produced a table of relativistic corrections for atoms. They used a spherically symmetric modified Slater potential for the spin-orbit term and numerical basis functions. Blume and Watson⁹ discussed a more exact treatment of the two-electron terms for atoms that would improve on the central field approximation. Hinkley *et al.*¹⁰ discussed the utility of Gaussian basis functions rather than exponential basis functions for atomic calculations. They found that Gaussian basis functions could be used and that Gaussians gave values for the spin-orbit parameter in agreement with those given by exponential functions contrary to some expectations.

We attempt to apply spin-orbit calculations to the Frenkel exciton in alkali halides. We also are attempting to discover whether we can accurately take into account additional relativistic effects, so that we may make future calculations in other large systems.

THEORY

We compute excitation energies by taking the differences between the energies of the ground and excited states. We obtain these energies by obtaining an approximate solution to Schrödinger's equation, $H\psi = E\psi$, using the Hartree-Fock technique and augmenting it by means of perturbation theory. We begin by making the Born-Oppenheimer approximation. We use the atomic system of units with $\hbar = e = m = 1$, where e is the electronic charge and m is the mass of the electron. The unit of energy is the hartree (1 hartree ≈ 27.2 eV). This is the most usual set of atomic units in use today.

In the Born-Oppenheimer approximation, the Hamiltonian is

$$\left[-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} \right] u_i(\mathbf{r}_1) + \sum_j \int d^3r_2 \frac{1}{r_{12}} |u_j(r_2)|^2 u_i(\mathbf{r}_1) - \sum_j \delta_{m_{s_i}, m_{s_j}} \int d^3r_2 \frac{1}{r_{12}} u_j^*(\mathbf{r}_2) u_i(\mathbf{r}_2) u_j(\mathbf{r}_1) = \varepsilon_i u_i(\mathbf{r}_1). \quad (2)$$

This equation may be derived using the usual variational technique.¹¹

When we calculate excitation energies, we use the UHF equation as a starting point and apply second-order Rayleigh-Schrödinger many-body perturbation theory (MBPT) according to the method of Beck and Kunz.¹² We shall consider here, for mathematical simplicity, the nondegenerate case without taking into account relativistic effects. Extension to degenerate system is simple although tedious.

We let $H = H_0 + V$. H_0 is the zero-order Hamiltonian, that is the sum over spaces of the one-electron Fock operators. V is the remainder of H and is the perturbation. Since the eigenstates of the complete Hamiltonian can be placed in one-to-one correspondence with eigenstates of the unperturbed Hamiltonian, we may select any one of the states to be perturbed and write

$$H|\psi_0\rangle = E_0|\psi_0\rangle \text{ and } H_0|\phi_0\rangle = W_0|\phi_0\rangle.$$

So,

$$\begin{aligned} E_0 &= W_0 + \langle \phi_0 | V | \phi_0 \rangle + \sum_{i(\neq 0)} \frac{\langle \phi_0 | V | \phi_i \rangle \langle \phi_i | V | \phi_0 \rangle}{W_0 - W_i} \sum_{j=0}^{\infty} \left[\frac{\langle \phi_i | V | \phi_i \rangle - \langle \phi_0 | V | \phi_0 \rangle}{W_0 - W_i} \right]^j \\ &= W_0 + \langle \phi_0 | V | \phi_0 \rangle + \sum_{i(\neq 0)} \frac{\langle \phi_0 | V | \phi_i \rangle \langle \phi_i | V | \phi_0 \rangle}{W_0 - W_i} \left[\frac{1}{1 - [\langle \phi_i | V | \phi_i \rangle - \langle \phi_0 | V | \phi_0 \rangle] / (W_0 - W_i)} \right]. \end{aligned} \quad (5)$$

Since we can expand to all orders we can find E to all orders and we can find $|\psi\rangle$. We can then say

$$H_1 = H + H_{\text{rel}},$$

$$\begin{aligned} H &= \sum_i -\frac{1}{2}\nabla_i^2 + \sum_I \sum_i \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{\substack{i,j \\ i < j}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \\ &+ \sum_{\substack{I,J \\ I < J}} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}, \end{aligned} \quad (1)$$

where i and j refer to electron coordinates and properties and I and J refer to ion coordinates and properties. The last term is a constant for a given geometry. In Eq. (1) the atomic units specified above are used. Z is the atomic number. We choose the wave function to be a single Slater determinant made up of one-electron orbitals $\phi(i)$, where $\phi(i) = \phi(r)\alpha$ or $\phi(i) = \phi(r)\beta$ where α and β are spinors. This wave function satisfies the Pauli exclusion principle. We use the unrestricted Hartree-Fock (UHF) formalism in which there are no symmetry or equivalence restrictions on the orbitals. The final state is not restricted to be an eigenstate of S^2 . The final state is an eigenstate of S_z , because the orbitals are chosen to be either spin up or spin down. The UHF equation is

$$E_0 = E_{\text{HF}} + \sum_{j(\neq 0)} \frac{1}{(W_0 - W_j)} \langle \phi_0 | V | \phi_j \rangle \langle \phi_j | V | \phi_0 \rangle. \quad (3)$$

If we replace the sum over states by a sum over orbitals, and let the occupied orbitals i and j be replaced by the virtual orbitals a and b in the state ϕ_j , one finds

$$E = E_{\text{HF}} + \frac{1}{4} \sum_{i,j}^{\text{occ}} \sum_{a,b}^{\text{virt}} \frac{|V_{ijab} - V_{ijba}|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}, \quad (4)$$

where

$$V_{ijab} = \langle \phi_i(1)\phi_j(2) | V | \phi_a(1)\phi_b(2) \rangle,$$

with

$$V = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|},$$

where the second term in Eq. (4) is not zero only for the proper spin combinations.

We can extend this derivation to all orders in perturbation theory.¹ If we keep only the dominant term in each order

where H_{rel} is the relativistic term. If we consider H_{rel} as a small perturbation we can compute the effects of H_{rel} using first-order perturbation theory. Usually most of the correlation energy can be included in the second-order

perturbation term, so we do not carry the series to all orders before including the relativistic corrections, but rather use the second-order perturbation energy and the Hartree-Fock wave function.

We shall now turn to the problem of finding the relativistic corrections to the Hamiltonian, which must be included in our perturbation theory.¹¹ We begin with the Dirac equation for a single particle of charge $-e$ in a potential ϕ . The Dirac equation is

$$[(E + \phi) - \boldsymbol{\alpha} \cdot \mathbf{c} \mathbf{p} - \beta c^2] \Psi = 0, \quad (6)$$

where

$$\Psi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$$

with ψ_1 and ψ_2 two component spinors, and

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

where $\boldsymbol{\alpha}$ and β are composed of 4×4 matrices. The matrices $\boldsymbol{\sigma}$ are the Pauli spin matrices. Now, we may expand the Dirac equation in powers of $(E' + \phi)/2c^2$. E' is the approximate value of E which results from our expansion. If we have ϕ spherically symmetry, we have

$$E' \psi_1 = -\frac{p^2}{2} \psi_1 - \phi \psi_1 - \frac{1}{8c^2} p^4 \psi_1 \\ - \frac{1}{4c^2} \boldsymbol{\sigma} \cdot \frac{1}{r} \frac{d\phi}{dr} \mathbf{r} \times \mathbf{p} \psi_1 + \frac{i}{4c^2} \nabla \phi \cdot \mathbf{p} \psi_1$$

or

$$E' \psi_1 = -\frac{p^2}{2} \psi_1 - \phi \psi_1 - \frac{1}{8c^2} p^4 \psi_1 \\ - \frac{1}{2c^2} \frac{1}{r} \frac{d\phi}{dr} \mathbf{S} \cdot \mathbf{L} \psi_1 + \frac{i}{4c^2} \nabla \phi \cdot \mathbf{p} \psi_1 \quad (7)$$

which we may write

$$E' \psi_1 = H_0 \psi_1 + H_{MV} \psi_1 + H_{s.o.} \psi_1 + H_D \psi_1. \quad (8)$$

These terms are the nonrelativistic Hamiltonian, the mass-velocity term, the spin-orbit term, and the Darwin term. We may transform $\nabla \phi \cdot \mathbf{p}$ into $\nabla^2 \phi$ which is the usual form of the Darwin term. In the system of units we use, we may write $(1/c) = \alpha$, where α is the fine-structure constant. We have neglected the effects which appear if electron-electron interactions are treated explicitly rather than by using an electrostatic potential.

We let $-V(r)$ be a centrosymmetric electrostatic, which is appropriate for an alkali halide due to their cubic lattice structure and write

$$\xi = \alpha^2 \int u^*(r) \frac{1}{r} \frac{dV}{dr} u(r) d^3r, \quad (9)$$

where ξ is the spin-orbit parameter and u is the wave function for an orbital solution to Eq. (2).

We make the approximation that integrals involving basis functions on different atomic sites are negligible. Kunz⁴ has discussed this problem for the alkali halides. He shows that for LiCl the integrals involving only one

site are much larger than the integrals involving different sites. So we may write

$$H_{s.o.} = \frac{\alpha^2}{2} \sum_I \sum_i \frac{1}{r} \frac{dV_I}{dr} l_i \cdot s_i, \quad (10)$$

where the I are the ions of a solid and the i are the electrons on the I th ion.

We choose

$$V_I(r) = - \left[\frac{Z}{r} - \frac{q(r)}{r} \right]. \quad (11)$$

We write

$$q(r) = \sum_i q_i(r),$$

where $q_i(r)$ is the charge in each orbital within a radius r . We note

$$q_i(r) = \int_0^r r_1^2 dr_1 \int d\Omega u_i^*(\mathbf{r}_1) u_i(\mathbf{r}_1). \quad (12)$$

We now consider the Darwin term. We observe

$$H_d = + \frac{\alpha^2 \pi}{2} [Z - q(r)] \delta(r) + \frac{\alpha^2}{8} \frac{1}{r} \nabla^2 [q(r)]. \quad (13)$$

The second term will be much smaller than the first term and may be neglected. We also observe that since $q(0) = 0$, the Darwin term will become

$$H_d = \frac{\alpha^2 \pi}{2} Z \delta(r). \quad (14)$$

We can rewrite the spin-orbit Hamiltonian

$$H_{s.o.} = \sum_i \xi_i(r) l_i \cdot s_i = \sum_i \xi_i l_i \cdot s_i, \quad (15)$$

where

$$\xi_i = \int r^2 dr u_i^*(r) \frac{1}{r} \frac{dV}{dr} u_i(r).$$

We may evaluate the matrix elements of $H_{s.o.}$ between the various unperturbed states. We use the intermediate coupling approximation as discussed by Condon and Shortley.¹³ We will make an approximation that we are dealing with atomic states. We need deal only with open shells, and we may write $H_{s.o.}$ in terms of ξ_l , where ξ_l is the spin-orbit parameter for the shell of angular momentum l . We consider only those states that have total angular momentum $J=1$, which therefore are reached by an electric dipole transition. We find that the crystal field is weak enough in comparison to the field due to the central ion that we may assume atomic selection rules hold. We note that $H_{s.o.}$ will mix states of different L and S , but that H_d and H_{MV} will not mix such states.

METHODS

We solve the UHF equation using the Roothaan procedure.¹⁴ We have used a new projection exclusion method recently developed by Kunz¹ to find excited states of specific symmetries.

We use the linear combination of atomic orbitals (LCAO's) technique. We set up clusters of atoms with the

nuclei in known positions and used atomic basis sets on each nucleus. For the alkali iodides, we used basis sets specially developed for ionic states from Huzinaga.¹⁵ Basis functions have been added to describe the excited states of the system, since the Huzinaga sets are only intended to describe the ground state. The added basis functions are variationally determined. Normally, we vary the values of the exponents of these functions by hand to minimize the energy of the triplet excited state. We varied these functions in a charge array of NaI, KI, LiI, and RbI, and in the entire system for CsI.

Integrals between the Gaussian basis functions used to expand the orbitals have been calculated using the POLYATOM code. The UHF and MBPT codes developed by Kunz and his co-workers¹⁶ have been used to find the Hartree-Fock energy and perform the MBPT calculation. Relativistic corrections were computed using the codes SPINORB, MASSVEL, and DARWIN we developed for this study.

The code SPINORB evaluates the term $\langle (1/r)(dV/dr) \rangle$ for selected orbitals. $V(r)$ is defined by

$$V(r) = \frac{Z}{r} - \frac{q(r)}{r}.$$

This is the same $V(r)$ we discussed above. We use $q(r)$ for all N electrons, not for $N - 1$. We sum over all ions.

The code DARWIN evaluates

$$u_i^*(0)u_i(0)$$

and sums it for all s orbitals.

The code MASSVEL evaluates

$$\int u^* \nabla^4 u d^3r$$

and sums it over all orbitals. All codes use Gaussian basis functions. We first transform from the basis set using real wave functions to a basis set using Y_l^m . We consider only s , p , and d functions. The radial parts of the integrals are evaluated analytically. We approximate the Darwin and mass-velocity terms by the terms computed for the $5p^45d$ and $5p^46s$ states of atomic iodine.

We computed all spectra for the alkali halides using a cluster of a halide ion surrounded by six alkali ions. This is a severe approximation for Li or NaI where the halogen-halogen overlap is high but reasonable for Rb or KI due to weak halogen-halogen overlap. The alkali basis sets were heavily contracted in free space.

The cluster was imbedded in a charge array. For crystals with NaCl structure we used a $5 \times 5 \times 5$ cube as the charge array. The cluster we study is located at the center. We represent the other ions as point charges. Each ion has six ions of opposite charge as nearest neighbors. The array is made charge neutral by adjusting the charges of the outermost ions. For crystals with CsCl structure, we use an array constructed by the program VXNNBR developed by Keegstra.¹⁷ The array contains the central ion and six shells of neighbors. We considered 113 sites in all. Each ion is surrounded by eight ions of opposite charge. We adjusted the charge of the outermost ions so the array is charge neutral.

The lattice parameter for CsI is from the data of Morlin.¹⁸ We took the lattice parameters for LiI and NaI

from Kunz.⁶ We found the lattice parameters for KI (Ref. 19) and RbI (Ref. 19) by extrapolation from high-temperature data using the coefficients of linear expansion given by White.²⁰

We ran Hartree-Fock calculations for LiI, NaI, and KI including all electrons in the cluster. We ran the Hartree-Fock calculations for RbI and CsI replacing the electrons of the alkali metal ions with pseudopotentials developed by Bachelet, Hamman, and Schlüter²¹ and implemented by Woodward.¹⁶ We were prevented by limitations on the amount of computer time available from doing all-electron MBPT calculations on any of the alkali iodides. We have therefore developed a version of MBPT which enables us to neglect core electrons. These states will not change much when a valence electron is excited and that differences in correlation energy will be small. For the iodides, we neglected all electrons but the $5s$ and $5p$ shells of the iodide ion.

We compute relativistic corrections using the Hartree-Fock wave functions. All operators are one electron operators, although the spin-orbit operator includes a sum over the charge density of all orbitals. The Darwin term is computed only for s states, since only these states have nonzero $\psi^*\psi$ at the origin. The term at the origin is the largest term. The mass-velocity term is computed for all orbitals. We found our correction terms by taking the difference between ground- and excited-state values for atomic iodine.

In the alkali halides we made corrections for the polarization of the ions surrounding the central halide ion by the multipole moment of the excited state. This is essentially a long-range correlation correction. We carried out the correction using the method of Mott and Littleton.²² Polarizabilities are taken from Tessman *et al.*²³ or from Jaswal and Sharma.²⁴

We have taken into account the electrostatic splitting of the $5p^55d$ exciton in the alkali iodides in the following manner. We first observe that this multiplet will split into F , D , and P states. However, our UHF wave functions are not eigenstates of L^2 for the p to d transition. We consider the case where we have two possible transitions p_x to d_{yx} or xyx and p_z to d_{xy} or xyz . If we decompose the real basis functions into spherical harmonics, we can show that

$$\begin{aligned} E_{xyx} &= \frac{8}{15}E_F + \frac{1}{6}E_D + \frac{3}{10}E_P, \\ E_{xyz} &= \frac{1}{3}E_F + \frac{2}{3}E_D. \end{aligned} \quad (16)$$

Slater²⁵ has shown that the splitting between the singlet and triplet states and between the xyx and xyz states may be expressed in terms of three numbers F_2 , G_1 , and G_3 , which are related to the Coulomb and exchange integrals found when computing $\langle H \rangle$. We can solve for these numbers. Slater further shows that differences between the singlet and triplet F , P , and D states may be expressed in the same way. We may use the equations above, along with our values of F_2 , G_1 , and G_3 , to solve for the energies of eigenstates of L^2 and S^2 .

In the electric field of the crystal the energy levels of the d_{xy} and $d_{x^2-y^2}$ orbitals will be slightly different, since the orbitals transform as different irreducible representa-

tions of the cubic group. We compute the splitting of the D state in the crystal field by finding the energy of the p_z to d_{zz} transition and using the values of F_2 , G_1 , and G_3 which are known from the d_{xy} transition. We use a mixture of zz and s basis functions to represent a $2z^2 - x^2 - y^2$ state since there is no other way to converge that state.

We made all computations using a FPS164 scientific computer with a VAX 750 host machine.

RESULTS

We have computed spin-orbit parameters for the chloride, bromide, and iodide ions in free space and compared them to the results in Kunz.⁴ The parameters are compared in Table I. We find that the parameters we compute are smaller than those Kunz obtained. We have used Gaussian basis functions rather than a numerical basis set as Kunz did, which accounts for the difference.²⁶ We have computed Darwin and mass-velocity parameters for several alkali metals. They are presented in Table II. The numbers are less than would be expected by extrapolation from the values in Herman and Skillman.⁸ This is to be expected as numerical basis functions give a better picture of the charge distribution than Gaussians do, especially at the origin where relativistic corrections are greatest. Our results for the alkali iodides are given in Table III. Spin-orbit parameters are in Table IV.

In the alkali iodides we have studied excitons arising in the $5p$ shell of the iodide ion. The data for LiI do not extend to low enough energies to enable us to observe the low-lying doublet structure, so no conclusions can be drawn from this spectrum. LiI is extremely hygroscopic and the spectra can depend greatly on the water absorbed, so no better data are available.

In NaI only a single pair of low-lying peaks is observed. We calculate a spin-orbit parameter less than that observed experimentally. We have neglected effects due to the second-nearest-neighbor iodide ions in computing the spin-orbit parameter. In NaI the outer shells of the iodide ions are in contact, therefore, this is not a good approximation. If we take the parameter calculated by Kunz,⁴ we can predict $5p^56s$ states having the right separation about 0.6 eV higher than the experimental peaks. There is a broadening of the upper peak which could be due to $5p^55d$ states, which we predict to be at about the same energy as the $5p^56s$ state. We calculated the energy for the $5p^56s$ states including second-nearest-neighbor ions for NaI using pseudopotentials on all Na^+ ions and on all but the central I^- ion but the lack of variational freedom on the outer ions in the cluster prevented any improvement in the calculated result. We believe the energy of this

TABLE I. Spin-orbit parameters for free halide ions.

Ion	This work (hartrees)	Kunz (Refs. 4 and 6) (hartrees)
$\text{Cl}^- 3p$	0.0027	0.0027
$\text{Br}^- 4p$	0.0102	0.0111
$\text{I}^- 5p$	0.0184	0.0232

TABLE II. Darwin and mass-velocity parameters for alkali metal atoms [basis sets of Woodward (Refs. 4 and 16)].

Orbital	Darwin term (hartrees)	Mass-velocity term (hartrees)
Li 1s	0.0016	-0.0019
Li 2s	0.00005	-0.00007
Na 1s	0.3481	-0.4314
Na 2s	0.0209	-0.0324
Na 2p		-0.0032
Na 3s	0.0005	-0.0007
K 1s	2.800	-3.547
K 2s	0.2396	-0.3973
K 2p		-0.0546
K 3s	0.0257	-0.0443
K 3p		-0.0060
K 4s	0.0010	-0.0017
Rb 1s	41.2876	-52.5161
Rb 2s	4.2618	-7.1989
Rb 2p		-1.1641
Rb 3s	0.6986	-1.2438
Rb 3p		-0.2402
Rb 3d		-0.0435
Rb 4s	0.0800	-0.1442
Rb 4p		-0.0225
Rb 5s	0.0034	-0.0061

state could be improved with a better basis set and by inclusion of second neighbor I^- ions.

In KI we predict a $5p^56s$ splitting less than that observed experimentally. The experimental and predicted values for the lower energy $5p^56s$ peak are within 0.1 eV but the values for the higher-energy peak differ by 0.2 eV. The energy predicted for the $5p^55d^3D$ peak is correct to within 0.2 eV, but the splitting in the crystal field is larger than predicted.

In RbI the predicted and experimental values of the lowest peak are within 0.1 eV. The values predicted for the three higher peaks agree best with experiment if the $5p^56s$ peak is lower in energy than the $5p^55d$ peaks, rather than higher in energy, as guessed in the experimental paper.

In CsI the predicted values are once again higher than the experimental values. The $5p^56s$ splitting appears correct. We predict the energy for one of the $5p^55d$ peaks correctly relative to the $5p^56s$, but the crystal-field splitting predicted is much too large. CsI is another system where a better basis set could probably improve the energies. In the CsI case, we do not treat all electrons in the cesium ions due to limitations on computer time, memory, and disk space. This means we cannot account for effects due to the overlap between cesium ion wave functions and iodide ion wave functions. Thus we are in a similar limitation as for LiI, NaI except here it is for Cs-I overlaps rather than I-I overlaps.

For the same reasons of computational difficulty, we are unable to include second-nearest-neighbor iodide ions in our cluster. As we mentioned in the Introduction, the small size of the sodium and lithium ions means that the iodide ion wave functions will overlap. We therefore ex-

TABLE III. Results for the lowest peaks of the alkali iodides. [The first column uses the spin-orbit parameter from Ref. 8. The second column uses the spin-orbit parameter from Kunz (Ref. 4). The third column is the experimental data.]

	Ref. 8 (eV)	Kunz (eV)	Expt. data (eV ²)
Lithium iodide			
$5p^5 6s^3 P$	7.43	7.32	peak 1: 6.75 ^a
$5p^5 6s^1 P$	8.24	8.48	peak 2: 7.1 ^a
$5p^5 5d^3 D_{xy}$	6.43		peak 3: 7.6 ^a
$5p^5 5d^3 D_{zz}$	7.00		
Sodium iodide			
$5p^5 6s^3 P$	6.28	6.19	peak 1: 5.6
$5p^5 6s^1 P$	7.07	7.27	peak 2: 6.7
$5p^5 5d^3 D_{xy}$	7.36		peak 3: 7.4
$5p^5 5d^3 D_{zz}$	7.13		
Potassium iodide			
$5p^5 6s^3 P$	6.14	6.04	peak 1: 5.9
$5p^5 6s^1 P$	6.90	7.10	peak 2: 6.7
$5p^5 5d^3 D_{xy}$	6.88		peak 3: 6.9
$5p^5 5d^3 D_{zz}$	6.80		peak 4: 7.3
Rubidium iodide			
$5p^5 6s^3 P$	5.71	5.63	peak 1: 5.7
$5p^5 6s^1 P$	6.50	6.67	peak 2: 6.5
$5p^5 5d^3 D_{xy}$	6.61		peak 3: 6.7
$5p^5 5d^3 D_{zz}$	6.98		peak 4: 7.0
Cesium iodide			
$5p^5 6s^3 P$	6.59		peak 1: 5.8
$5p^5 6s^1 P$	7.38		peak 2: 5.9
$5p^5 5d^3 D_{xy}$	6.74		peak 3: 6.0
$5p^5 5d^3 D_{zz}$	8.07		peak 4: 6.8

^aReference 6.

pect our results for NaI and LiI to be poorer than for KI and RbI. In fact, our results agree with our expectations, and the enhanced splitting is not observed. In addition, our energies are too high for LiI and NaI. The same analysis applies to CsI due to the neglect of cesium and iodide orbital overlap.

TABLE IV. Spin-orbit parameters for I⁻ ions (5*p* orbital).

Material	Parameter (hartree)
free I ⁻	0.0232 ^a
LiI $p \rightarrow s$	0.0208
LiI $p \rightarrow d$	0.0208
NaI $p \rightarrow s$	0.0204
NaI $p \rightarrow d$	0.0208
KI $p \rightarrow s$	0.0200
KI $p \rightarrow d$	0.0206
RbI $p \rightarrow s$	0.0205
RbI $p \rightarrow d$	0.0206
CsI $p \rightarrow s$	0.0203
CsI $p \rightarrow d$	0.0209

^aReference 4.

CONCLUSIONS

The methods used here give good results predicting the energy levels of alkali iodide crystals for excitations from valence states. It appears that we can explain the lowest excitations in the alkali iodide spectra satisfactorily using a localized excitation model. We can also compute spin-orbit parameters accurately for the cases where overlap between the wave functions of ions of the same type is not large. In NaI, where the overlap is large, we cannot obtain the correct spin-orbit parameter, but we can still compute the correct spin-orbit splitting if the correct spin-orbit parameter is used. It is clear that we must include spin-orbit coupling to get any meaningful results on the alkali iodides.

Our values for the Darwin term and the mass-velocity term are not as accurate as those for the spin-orbit parameter because the Gaussian basis set does not well represent the wave function at the origin.

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¹P. W. Goalwin and A. B. Kunz, Phys. Rev. B **34**, 2140 (1986).

²K. Teegarden and G. Baldini, Phys. Rev. **155**, 896 (1967).

³J. C. Phillips, Phys. Rev. A **136**, 1705 (1964).

⁴A. B. Kunz, Phys. Rev. **159**, 738 (1967).

⁵Y. Onodera, and M. Okazaki, J. Phys. Soc. Jpn. **21**, 1273 (1966).

⁶A. B. Kunz, Phys. Rev. **151**, 620 (1966); **180**, 934 (1969).

⁷Y. Osaka, Y. S. Osaka, and F. Goto, J. Phys. Soc. Jpn. **17**, 1715 (1962).

⁸F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice Hall, Englewood Cliffs, N.J., 1963).

⁹M. Blume and R. E. Watson, Proc. R. Soc. London, Ser. A **270**, 127 (1962); **271**, 565 (1963).

¹⁰R. K. Hinkley, T. E. H. Walker, and W. K. Richards, J. Chem. Phys. **62**, 5975 (1970).

¹¹H. A. Bethe and R. Jackiw, *Intermediate Quantum Mechanics* (Cummings, Reading, MA, 1968).

¹²D. R. Beck and A. B. Kunz, J. Phys. B **17**, 2159 (1984).

¹³E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University, Cambridge, 1935), p. 266.

¹⁴C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951); **32**, 179 (1960).

¹⁵S. Huzinaga *et al.*, *Gaussian Basis Sets for Molecular Calculations* (Elsevier, Amsterdam, 1984).

¹⁶J. C. Boisvert, Ph.D. thesis, University of Illinois, 1984 (unpublished); N. C. Bacalis, Ph.D. thesis, University of Illinois,

- 1984 (unpublished); C. Woodward, Ph.D. thesis, University of Illinois, 1986 (unpublished).
- ¹⁷P. B. Keegstra (private communication).
- ¹⁸Z. Morlin, *Acta Cryst.* **B27**, 2493 (1971).
- ¹⁹JCPOS, *Powder Diffraction File, Inorganic Phases* (International Center for Diffraction Data, Swarthmore, PA, 1982).
- ²⁰G. A. White, *Proc. R. Soc. London, Ser. A* **286**, 204 (1965).
- ²¹G. Bachelet, D. R. Hamman, and M. Schluter, *Phys. Rev. B* **26**, 4199 (1982).
- ²²N. F. Mott and M. J. Littleton, *Trans. Faraday Soc.* **34**, 485 (1938).
- ²³J. R. Tessman, A. H. Kahn, and W. Shockley, *Phys. Rev.* **92**, 890 (1953).
- ²⁴S. S. Jaswal and T. P. Sharma, *J. Phys. Chem. Solids* **34**, 509 (1973).
- ²⁵J. C. Slater, *Quantum Theory of Matter* (McGraw-Hill, New York, 1951), p. 486ff.
- ²⁶J. E. Eby, K. J. Teegarden, and D. B. Dutton, *Phys. Rev.* **116**, 1099 (1959).