

## Exciton states in solid rare gases

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The problem of the exciton states in solid rare gases is studied within the framework of the integral-equation approach appropriate for intermediate-coupling interaction. The different contributions appearing in the integral equation are investigated and related to physical quantities by means of an analysis of their behavior in the two limiting situations in which the effective-mass approximation (EMA) or the atomic solution holds. An approximate solution is given for the intermediate case using the simplest trial wave functions having the correct behavior in both limits. Quantitative results, obtained by this simple approach, are remarkably more accurate than both the EMA and the atomic values.

### I. INTRODUCTION

Solid rare gases are the simplest molecular solids, hence the importance of the study of their electronic properties. Rare-gas elements are closed-shell systems with zero valence; the atoms are bound in the solid by weak Van der Waals interactions. The lattice spacings  $a_0$ , or equivalently the radii of the central cells  $\rho_{cc}$  (we define  $\rho_{cc}$  as the radius of a sphere whose volume  $\Omega = \frac{1}{4} a_0^3$  is that of the primitive cell) are, consequently, large compared to those of other materials. Under such conditions it is expected that the valence bands are flat because the overlaps between atomiclike orbitals centered on different atoms are small. At the same time the conduction bands are free-electron-like, with an effective mass  $\mu$  of the order of unity.<sup>1</sup> Because of these properties of the valence and conduction bands, it has been possible to find methods and basis functions giving an adequate picture of these states.<sup>2</sup> For the excitons we expect similarly an atomiclike behavior for the tightly bound lowest levels, and a hydrogeniclike behavior for the spread-out higher-energy states. The parameter characterizing the former is still  $\rho_{cc}$ , while those appropriate to the latter are  $\mu$  and the dielectric constant  $\epsilon_0$ , which is also of the order of unity. It turns out that this distinction is only approximate, and some states definitely occur in a region of intermediate coupling. In Sec. II we point out that the formula

$$E_{\text{EMA}}(n) = E_g - B/n^2 = E_g - \mu/2\epsilon_0 n^2, \quad (1)$$

giving the energies of the exciton states in the effective-mass approximation (EMA), gives a fit within 0.02 eV to the experimental transition energies, except for those of the lowest ( $n=1$ ) states. The defect  $\Delta$ , defined as the difference between the experimental and the EMA values for the  $n=1$  states

$$\Delta = E_{\text{expt}} - E_{\text{EMA}} \quad (2)$$

is positive and about 1 and 0.2 eV in solid Ne and Ar, respectively. The energies of the first atomic transitions  $E_A$  are also about 0.9 and 0.4 eV lower than the corresponding energies  $E_{\text{expt}}$  in solid Ne and Ar. Thus we conclude that the lowest exciton levels are neither hydrogeniclike nor atomiclike. But we still have to understand in what sense they are intermediately coupled, because any kind of average between  $E_{\text{EMA}}$  and  $E_A$  would be lower than  $E_{\text{expt}}$ . If we consider solid Kr and Xe the defect  $\Delta$  becomes 0.06 and 0.00 eV, respectively. Thus we must understand why  $\Delta$  is large in Ne and Ar and small or null in Kr and Xe.

In recent years considerable effort has been exerted to solve the exciton problem for intermediate coupling. Several authors<sup>2-8</sup> have provided the theoretical framework and carried out quantitative studies for the elements of the sequence. We consider here, in particular, the integral-equation approach.<sup>5,7,8</sup> Complete calculations within this framework require detailed knowledge of the band structures and are addressed to specific examples separately. We study first the general solution of the integral equation and establish its connection to the known exact solutions in the limiting cases of extended and localized states, namely, the EMA and the atomic solutions, respectively. In performing such a study, given in Sec. III, we relate the terms of the integral equation to well-defined physical entities, and better understand the assumptions and approximations of calculations based on this approach. Subsequently, we give an approximate solution to the problem by taking the simplest trial wave functions which have the proper behavior in both limits. We thus obtain in a simple fashion a direct quantitative explanation of the meaning and of the trend of the defect  $\Delta$  in the rare-gas solids. We report these results in Sec. IV.

TABLE I. Experimental transition energies in eV. Data from Refs. 9 and 10. The notations are described in the text.

$J$	Ne <sup>+</sup> <sup>a</sup> (8 K)		Ar (20 K)		Kr (20 K)		Xe (20 K)	
	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$
$E_{\text{expt}} n=1$	17.59		12.06		10.17		8.37	
$E'_{\text{expt}}$ 1'		17.79		12.24		10.86		9.51
2	20.25		13.57		11.23		9.07	
2'		20.37		13.75		11.92		
3	20.92		13.89		11.44		9.21	
3'		21.02		14.07*		12.21(?)		
4	21.18		13.97		11.52			
4'		21.24(?)						
5	21.29							
$E_A$	16.671		11.624		10.033		8.437	
$E'_A$		16.848		11.828				

<sup>a</sup>“+” denotes reflection data. A prime refers to the  $J = \frac{1}{2}$  series.

## II. EXPERIMENTAL SITUATION

In Table I we report recent data taken from Saile *et al.*<sup>9</sup> on the experimental energies of the lower exciton transitions in solid Ne, Ar, Kr, and Xe. These results, obtained at Deutsches Elektronen-Synchrotron (DESY) using synchrotron radiation and high-resolution techniques, are probably the most accurate to date, the probable error being less than or equal to 0.01 eV (a review of the previous experimental work can be found in Ref. 2). Two series are detected and denoted by  $\frac{3}{2}$  and  $\frac{1}{2}$ . They arise from  $\Gamma_{15}$  exciton states with  $s$ -type envelope functions, converging, respectively, to the limits  $E_g$  and  $E'_g$ . These limits, which are the onsets of the interband transitions, correspond to a free electron-hole pair, with the electron in the mini-

um of the conduction band and the hole in either of the maxima of the spin-orbit-split valence bands  $\Gamma_8^-$  and  $\Gamma_6^-$ . In the last two rows of Table I we reproduce the lowest experimental atomic transition energies  $E_A$  and  $E'_A$  taken from Moore.<sup>10</sup> They arise from the lowest  $P_1$  atomic excited states. The corresponding series would converge to the limits  $E_{IA}$  or  $E'_{IA}$ , the ionization potentials of the free atom in which the positive ion is left in either the  $J = \frac{3}{2}$  or  $J = \frac{1}{2}$  states. The energies  $E_A$  and  $E_{IA}$  are related to  $E_{\text{expt}}$  and  $E_g$ , respectively, in the solid phase.

In Table II we fit the experimental energies of Table I with the EMA series (1). The two parameters  $E_g$  and  $B$  of the EMA are also given, as well as the defect  $\Delta$  defined in Eq. (2).

In Table III we give the central-cell radii  $\rho_{cc}$

TABLE II. Effective-mass approximation energies and other parameters in eV, for the rare-gas solids. The symbols are defined in the text.

$J$	Ne		Ar		Kr		Xe	
	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$
$E_{\text{EMA}} n=1$	16.51		11.86		10.11		8.37	
$E'_{\text{EMA}}$ 1'		16.90		12.04		11.23		9.07
2'	20.25		13.57		11.23		9.07	
2		20.37		13.75		11.92		
3	20.94		13.89		11.44		9.21	
3'		21.02		14.07		12.21(?)		
4	21.18		13.99		11.52			
4'		21.24						
5	21.29							
$E_g$	21.49		14.14		11.61		9.31	
$E'_g$		21.53		14.32				
$B$	4.98		2.28		1.50		0.94	
$B'$		4.63		2.28				
$\Delta$	1.08		0.2		0.06		0.00	
$\Delta'$		0.89		0.2				

TABLE III. Central cell and EMA radii in a.u. and dielectric constants taken from Refs. 11-13.

$J$	Ne		Ar		Kr		Xe	
	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$
$\rho_{cc}$	3.27		3.918		4.175		4.533	
$\epsilon_0$	1.24		1.660		1.882		2.217	
$\rho'_{EMA}$	2.20		3.595		4.820		6.529	
$\rho_{EMA}$	2.37		3.595					

and the dielectric constants  $\epsilon_0$ ,  $\rho_{cc}$  and  $\epsilon_0$  are derived for solid Ne from the lattice spacing and the atomic polarizability given in the book by Kittel.<sup>11</sup> The Clausius-Mossotti equation is used to obtain  $\epsilon_0$ . The quantities  $\rho_{cc}$  for solid Ar, Kr, and Xe are obtained from data available in the literature<sup>12</sup> for a temperature of 20 K. The dielectric constants  $\epsilon_0$  are taken from a paper by Sinnocch and Smith.<sup>13</sup> The last two rows of Table III give the EMA radii  $\rho_{EMA}$ , obtained from

$$\rho_{EMA} = \epsilon_0 / \mu. \quad (3)$$

### III. INTEGRAL EQUATION

The general integral equation for exciton states with wave vector  $\vec{k}_{exc} = 0$  from singly excited Slater determinants can be written<sup>2,5,7,8,14</sup>

$$[E_c(\vec{k}) - E_v(\vec{k}) - E] A_{c,v}(\vec{k}) + \sum_{c',v'} \sum_{\vec{k}'} U_{c,v,c',v'}(\vec{k}, \vec{k}', \vec{k}_{exc}) A_{c',v'}(\vec{k}') = 0, \quad (4)$$

where

$$U = -\langle \psi_{c\vec{k}} \psi_{v\vec{k}'} | \frac{e^2}{r_{12}} | \psi_{c\vec{k}} \psi_{v\vec{k}'} \rangle + \lim_{\vec{k}_{exc} \rightarrow 0} \langle \psi_{c\vec{k}+\vec{k}_{exc}} \psi_{v\vec{k}'} | \frac{e^2}{r_{12}} | \psi_{v\vec{k}} \psi_{c'\vec{k}'+\vec{k}_{exc}} \rangle, \quad (5)$$

and  $E_v(\vec{k})$ ,  $E_c(\vec{k})$ ,  $\psi_{v\vec{k}}$ ,  $\psi_{c\vec{k}}$  are the valence- ( $v$ ) and conduction- ( $c$ ) band energies and the corresponding Bloch functions. These can be the solutions of a Hartree-Fock-type calculation. The integration in Eq. (5) includes summation over the spin variables. The limit  $\vec{k}_{exc} \rightarrow 0$  depends on the orientation of that vector.

Following Altarelli and Bassani<sup>5</sup> we expand the kernel (5) in Wannier functions (WF's)  $a_i(\vec{r} - \vec{R})$ , where  $i = v, c$  and  $\vec{R}$  is a vector of the lattice. The bielectronic four-center integrals

$$\langle a_i a_{i''} | \frac{e^2}{r_{12}} | a_{i'} a_{i''} \rangle = \int \int d\vec{r}_1 d\vec{r}_2 a_i^*(\vec{r}_1) a_{i'}(\vec{r}_1 - \vec{R}') \times \frac{e^2}{r_{12}} a_{i''}^*(\vec{r}_2 - \vec{R}'') a_{i''}(\vec{r}_2 - \vec{R}''') \quad (6)$$

occur in the analysis. In order to evaluate the relative magnitude of these integrals we use a method suggested by Kunz<sup>15</sup> which is suitable for all localized orbitals. It consists in considering the integrations over  $\vec{r}_1$  and  $\vec{r}_2$  as separate, ignoring the coupling term  $e^2/r_{12}$ . We then classify the matrix elements according to their order in terms of the overlap integrals

$$\int d\vec{r} a_i^*(\vec{r}) a_i(\vec{r} - \vec{R}). \quad (7)$$

We deduce that the integrals (6) are of zero order if  $\vec{R}' = 0$  and  $\vec{R}'' = \vec{R}'''$ , of first order if  $\vec{R}' \neq 0$  and  $\vec{R}'' = \vec{R}'''$  or  $\vec{R}' = 0$  and  $\vec{R}'' \neq \vec{R}'''$ , and of second order if  $\vec{R}' \neq 0$  and  $\vec{R}'' \neq \vec{R}'''$ . The factor  $e^2/r_{12}$  couples the integrations over  $\vec{r}_1$  and  $\vec{r}_2$ , but is, of course, of long range, so that it does not change the order in overlap of the total integral. In our case the overlap integral (7) is not only a small number compared to unity when  $\vec{R} \neq 0$ , but it is exactly zero, because of the orthogonality of the WF's. Thus, we consider only the terms with  $\vec{R} = 0$  and  $\vec{R}'' = \vec{R}'''$ . Terms such as

$$\langle a_c a_{v\vec{R}} | \frac{e^2}{r_{12}} | a_{v\vec{R}} a_c \rangle$$

are sometimes considered,<sup>2</sup> but they are of second order and can be neglected. On the other hand, terms like

$$Q(\vec{R}) = \langle a_c a_{v\vec{R}} | \frac{e^2}{r_{12}} | a_c a_{v\vec{R}} \rangle, \quad (8)$$

the electron-hole Coulomb interaction, are neglected for  $\vec{R} \neq 0$  in the one site approximation.<sup>7,8</sup> The reliability of this approximation does not depend on the localization of the WF's. In fact, in the case of extremely localized WF's

we get for  $\vec{R} \neq 0$ ,

$$Q(R) = e^2/R, \quad (9)$$

which is in our analysis a zero-order long-range term. We conclude that the terms (8) with  $\vec{R} \neq 0$  must generally be considered, unless the extension of the envelope function is much smaller than  $\rho_{cc}$ .

We use a model involving two simple  $s$ -like bands and singlet excitons. This simplifies the formalism and the discussion. The final results apply also to the case of solid rare gases, in which  $p$ -type valence bands and spin mixing occur, provided that we neglect the interaction between the partners of each spin-orbit doublet and consider the  $\frac{3}{2}$  and  $\frac{1}{2}$  series to be independent. The proper generalization to  $2 \times 2$  matrices to include these effects, which is not carried out here, is, however, straightforward.<sup>7,8</sup>

With the previous assumptions the kernel (5) is given by

$$U = -\frac{1}{N} \mathcal{G} - \frac{1}{N} \sum_{\vec{R} \neq 0} e^{i(\vec{k} - \vec{k}') \cdot \vec{R}} Q(\vec{R}), \quad (10)$$

$$\det \left| \delta_{\vec{R}\vec{R}'} - N^{-1} \delta_{\vec{R}} \mathcal{G} \sum_{\vec{R}} \frac{e^{i\vec{k} \cdot \vec{R}}}{E_c(\vec{k}) - E_v(\vec{k}) - E} - N^{-1} (1 - \delta_{\vec{R}}) Q(-\vec{R}) \sum_{\vec{R}} \frac{e^{i\vec{k} \cdot (\vec{R} - \vec{R}')}}{E_c(\vec{k}) - E_v(\vec{k}) - E} \right| = 0. \quad (15)$$

However, if we suppose in the derivation that the envelope function  $F(\vec{R})$  is null for  $\vec{R} \neq 0$ , the third term in Eq. (15) does not appear, and we obtain

$$1 - N^{-1} \mathcal{G} \sum_{\vec{R}} \frac{1}{E_c(\vec{k}) - E_v(\vec{k}) - E} = 0. \quad (16)$$

This is called the one-site approximation, because the electron and the hole are both confined to the central cell. Equation (16) has been solved<sup>7,8</sup> for solid Ar and Ne making use of WF's,  $\mathcal{G}$  and  $\sum_{\vec{k}} [E_c(\vec{k}) - E_v(\vec{k}) - E]^{-1}$  having been obtained from previous band structure calculations.

Multiplying Eq. (4) with kernel (10) by  $e^{-i\vec{k} \cdot \vec{R}}$ , and summing over  $\vec{k}$  yields

$$\sum_{\vec{k}} [E_c(\vec{k}) - E_v(\vec{k})] e^{-i\vec{k} \cdot \vec{R}} A(\vec{k}) - \delta_{\vec{R}} \mathcal{G} F(0) - (1 - \delta_{\vec{R}}) Q(-\vec{R}) F(\vec{R}) = E F(\vec{R}). \quad (17)$$

Let us suppose that the envelope function  $F(\vec{R})$  extends over several cells, and therefore that  $A(\vec{k})$  is sharply peaked in  $\vec{k}$  space. We now develop  $E_c(\vec{k}) - E_v(\vec{k})$  near its minimum in  $\vec{k}$  space in the form

$$E_c(\vec{k}) - E_v(\vec{k}) = E_g + (1/2\mu)k^2, \quad (18)$$

where  $N$  is the number of primitive cells and

$$\mathcal{G} = Q(0) - 2J(0) - 2S_{LT}. \quad (11)$$

in Eq. (11),

$$J(\vec{R}) = \langle a_c a_{v\vec{R}} | \frac{e^2}{r_{12}} | a_v a_{c\vec{R}} \rangle \quad (12)$$

is the electron-hole exchange interaction, and

$$S_{LT} = \lim_{\vec{k}_{\text{exc}} \rightarrow 0} \sum_{\vec{R} \neq 0} e^{i\vec{k}_{\text{exc}} \cdot \vec{R}} J(\vec{R}) \quad (13)$$

is the dipole-dipole interaction term, representing a charge transfer between different atoms and responsible for the longitudinal-transverse splitting.<sup>7,8,16</sup>

Taking now Eq. (4) with kernel (10), multiplying by  $e^{-i\vec{k} \cdot \vec{R}}$ , dividing by  $E_c(\vec{k}) - E_v(\vec{k}) - E$  and summing over  $\vec{k}$ , a set of linear equations for the unknown

$$F(\vec{R}) = \sum_{\vec{k}} e^{i\vec{k} \cdot \vec{R}} A(\vec{k}), \quad (14)$$

results, having nontrivial solutions when

and use the approximation

$$Q(R) = e^2/\epsilon_0 R, \quad R \neq 0 \quad (19)$$

for the screened Coulomb interaction. Letting  $\vec{R}$  become the continuous variable  $\vec{r}$  and neglecting the short-range second term in Eq. (17), we find the effective mass equation

$$E_g F(\vec{r}) - \frac{1}{2\mu} \nabla^2 F(\vec{r}) - \frac{e^2}{\epsilon_0 r} F(\vec{r}) = E F(\vec{r}) \quad (20)$$

for the envelope function  $F(\vec{r})$ . The eigenvalues of Eq. (20) are given by Eq. (1). The extension of  $F(\vec{r})$  can be regarded as the mean value of  $r$ ,

$$\langle r \rangle = \frac{1}{2} \rho_{\text{EMA}} [3n^2 - l(l+1)], \quad (21)$$

with  $\rho_{\text{EMA}}$  given by Eq. (3). From Eq. (21) and the data of Table III we conclude that  $\langle r \rangle$  is large compared to  $\rho_{cc}$  for  $n > 1$ , and therefore the EMA must work reasonably well.

Let us now consider the opposite situation, in which the envelope function  $F(\vec{R})$  is concentrated in the central cell. Such a situation can be imagined as arising from an expansion of the lattice spacing  $a_0$ . The third term in Eq. (17) disappears.  $S_{LT}$  in Eq. (13) vanishes and  $\mathcal{G}$ , from Eq. (11), becomes the atomic binding energy  $\mathcal{E}_A$  of the

excitation with respect to the ionization potential  $E_{IA}$ , as given in the single-transition approximation.<sup>17</sup> The factor  $E_c(\vec{k}) - E_v(\vec{k})$  can be developed in powers of  $\vec{k}$ , but as  $\rho_{cc}$  increases, the diameter of the Brillouin zone decreases as  $\rho_{cc}^{-1}$ . In this limit  $E_c(\vec{k}) - E_v(\vec{k})$  reduces to  $E_{IA}$ . Then Eq. (17) becomes

$$E = E_{IA} - \mathcal{G}_A. \quad (22)$$

In principle more conduction bands should have been included in the model, within a total width of the order of  $\mathcal{G}_A$ . But Eq. (22), giving the experimental atomic limit, is, of course, generally valid, provided that we consistently approximate  $\mathcal{G}_A$  with the eigenvalue of a Tamm-Dancoff matrix including all the conduction bands of the model.

Now, substituting in Eq. (17) the inverse transform

$$A(\vec{k}) = \frac{1}{N} \sum_{\vec{R}'} e^{-i\vec{k}\cdot\vec{R}'} F(\vec{R}'), \quad (23)$$

multiplying by  $F^*(\vec{R})$  and summing over  $\vec{R}$ , we are led to

$$E = \left( \frac{1}{N} \sum_{\vec{k}} [E_c(\vec{k}) - E_v(\vec{k})] \right. \\ \left. \times \sum_{\vec{R}, \vec{R}'} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')} F^*(\vec{R}) F(\vec{R}') \right. \\ \left. - \sum_{\vec{R} \neq 0} Q(-\vec{R}) |F(\vec{R})|^2 - \mathcal{G} |F(0)|^2 \right) \\ \times \left( \sum_{\vec{R}} |F(\vec{R})|^2 \right)^{-1}. \quad (24)$$

The one-site approximation yields

$$E = \frac{1}{N} \sum_{\vec{k}} [E_c(\vec{k}) - E_v(\vec{k})] - \mathcal{G}. \quad (25)$$

Like Eq. (16), Eq. (25) is based on the approximation that  $F(\vec{R}) = 0$  outside the central cell, but also has the advantage of greater simplicity. The observed values of  $E_{\text{expt}}$ , which are higher than  $E_A$ , are approximated by the solutions of Eq. (16), and also by those of Eq. (25), because atomic-type binding energies  $\mathcal{G}$  are substantially subtracted from the mean value over the Brillouin zone of  $E_c(\vec{k}) - E_v(\vec{k})$ , which is higher than  $E_g$  and  $E_{IA}$ . This is one of the important solid state effects. The other, the screened Coulomb interaction between the electron and the hole on that part of the envelope function outside the central cell, is not included. In Sec. IV we introduce this effect in a simple but meaningful way.

#### IV. APPROXIMATE SOLUTIONS OF THE INTERMEDIATE-COUPPLING EQUATION

Let us return to Eq. (24). An approximate expression of it having the same behavior in the two limiting cases discussed here is

$$E = \left[ \sum_{\vec{R} \neq 0} \left( E_g |F(\vec{R})|^2 + \langle F(\vec{R}) | T | F(\vec{R}) \rangle - \frac{e^2}{\epsilon_0 R} |F(\vec{R})|^2 \right) \right. \\ \left. + E_A |F(0)|^2 \right] \left( \sum_{\vec{R}} |F(\vec{R})|^2 \right)^{-1}, \quad (26)$$

where the second term in the first large parentheses is the mean value of the kinetic energy outside the central cell. Of course, the difficulty with Eqs. (24) and (26) is that we do not know the function  $F(\vec{R})$  in the intermediate case. We use a trial function  $f(\vec{r})$  of the continuous variable  $\vec{r}$  of the simplest possible form and having the behavior of  $F(\vec{R})$  in the limiting cases, i.e.,  $f(\vec{r})$  must be constant for  $r \leq \rho_{cc}$  and hydrogenic for  $r \geq \rho_{cc}$ . We require that it be continuous at  $r = \rho_{cc}$  [the continuity of the derivative is not necessary because Eq. (26) involves only integrated quantities]. Then we have, for the lowest state,

$$f(r) = \begin{cases} 1 & \text{for } r \leq \rho_{cc}, \\ \exp(\rho_{cc}/\rho) \exp(-r/\rho) & \text{for } r \geq \rho_{cc}, \end{cases} \quad (27)$$

where  $\rho$  is a parameter giving the extension of  $f(r)$  and to be specified later. Replacing summations by integrals of the form

$$\sum_{\vec{R}} \rightarrow \frac{3}{4\pi\rho_{cc}^3} \int d\vec{r}, \quad (28)$$

we obtain, using Eqs. (26) and (27), the result

$$E = \frac{E_A + \alpha E_g + \beta(1/\mu\rho_{cc}^2) - \gamma e^2/\epsilon_0\rho_{cc}}{1 + \alpha}. \quad (29)$$

In Eq. (29) the quantities  $\alpha$ ,  $\beta$ , and  $\gamma$  are

$$\alpha = \frac{3}{2} (x + x^2 + \frac{1}{2} x^3),$$

$$\beta = \frac{3}{4} [1 - (1/x) + \frac{1}{2} x],$$

$$\gamma = \frac{3}{2} (x + \frac{1}{2} x^2),$$

where  $x = \rho/\rho_{cc}$ . Furthermore, we can introduce in Eq. (29) a different effective mass  $\mu'$ , related to  $\rho$  by the hydrogenic relation

$$\rho = \epsilon_0/\mu'. \quad (30)$$

Under such condition the kinetic and potential energies are no longer independent and Eq. (29) further simplifies to

$$E = \frac{E_A + \alpha(E_g - e^2/2\epsilon_0\rho)}{1 + \alpha}. \quad (31)$$

TABLE IV. Energies obtained using Eqs. (31) and (29) in eV.

$J$	Ne		Ar		Kr		Xe	
	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$
$E$ (31)	17.83		11.96		10.10		8.378	
$E'$ (31)		17.90		12.14				
$E$ (29)	17.65		11.93					
$E'$ (29)		17.75		12.12				

It is easy to verify that both Eq. (29) and (31) have the previously discussed behavior for  $\rho_{cc} \ll \rho \rightarrow \rho_{EMA}$  and  $\rho \ll \rho_{cc}$  and that, for instance, in Eq. (31),  $E$  lies between  $E_A$  and the hydrogenic energy  $E_g - e^2/2\epsilon_0\rho$ .

It is now necessary to decide what is  $\rho$  in the actual intermediate case. The appropriate choice is between  $\rho_{cc}$  and  $\rho_{EMA}$ , depending on whether we wish to give the envelope function a predominantly EMA or atomic-type behavior. As we see in Table III,  $\rho_{EMA}$  is larger than  $\rho_{cc}$  in Kr and Xe, while it is smaller in Ne and Ar. We therefore suppose the EMA behavior to adequately describe the situation in Kr and Xe, while the atomiclike characteristics predominate in Ne and Ar. In the first case, Eqs. (31) and (29) coincide and have the meaning of an EMA solution weakly perturbed in the central cell. We do not see this effect at the present stage of approximation because the EMA fits exactly the three data in Xe within their accuracy, and it is a few hundredths of an eV below  $E_{expt}$  in Kr. Then the values given by Eq. (31), and exhibited in Table IV, have the same accuracy as the EMA. The situation is rather different in Ne and Ar, where the EMA fails significantly. Choosing  $\rho = \rho_{cc}$ , Eqs. (29) and (31) assume the meaning of an atomic solution perturbed by a hydrogenic effective Hamiltonian outside the central cell. Equation (31), in particular, becomes also independent of  $\mu$ . We see in Table IV that it provides an improvement by one order of magnitude in the values of  $E_{EMA}$  and  $E_A$  in Ne, and by factors of 2 and 4 for  $E_{EMA}$  and  $E_A$ , respectively, in Ar. Equation (29) provides even more accurate results in solid Ne, a few hundredths of an eV from  $E_{expt}$ . Of course, the failure of the EMA, particularly in Ne, is due to the fact that  $\rho_{EMA}$  is small compared to  $\rho_{cc}$ , and to the artificial concentration of the EMA solution inside the atom. Conversely,  $E_A$  lies below  $E_{expt}$  because in the solid the interaction between the electron and the hole is screened by

$\epsilon_0$  outside the central cell. We conclude that  $\rho_{EMA}$  would be appropriate if corrections to higher components of the series were considered, but  $\rho_{cc}$  is the correct value for  $\rho$  for the lowest state. Finally we mention that, even though we are not using semiempirical parameters, choices slightly different from those made would be possible leading to the same limiting situations. We could, for instance, choose  $\rho = 0.5d$ , where  $d$  is the nearest-neighbor distance ( $\rho = 0.9\rho_{cc}$  in this case) or some intermediate value between  $0.5d$  and  $\rho_{cc}$ . In the case of Ne the results of Eq. (31) or (29) remain well concentrated around  $E_{expt}$ , while in Ar they move toward  $E_{EMA}$ , because  $\rho$  becomes more comparable to  $\rho_{EMA}$ .

A blue shift of the order of 1 eV with respect to the vapor-phase values  $E_A$  is also found in other molecular solids, such as solid  $H_2$  and  $H_2O$  (see, for instance, Refs. 18 and 19). Equation (31) can then provide a quantitative evaluation of it, without a direct knowledge of the EMA parameters ( $E_g$  can be obtained from photoconductivity experiments, or, if not available, from a reasonable estimate from the optical data and band calculations). Equation (31), or its generalizations, can also be useful in the study of core-excitons and impurities states.

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- <sup>1</sup>In this paper we use the atomic system of units, in which  $\hbar$ ,  $e$ , and  $m$  are unity. However, the numerical values of the energies will be given in eV.
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