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Valence excitons and inner-shell excitons in gaseous and solid argon

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Valence excitons from the 3*p* shell and core excitons from the 3*s* and 2*p* shells in gaseous and solid argon are studied within the envelope-function formalism. First, semiempirical model potentials for atomic excitons are considered; then solid-state effects, which include band structure and electron-hole screening, are taken into account. The problem of a sufficiently accurate account of the "band kinetic operator" is solved with first-order perturbation theory. A new interpretation of the excitonic spectrum originating from the 2*p* shell is given in terms of first-class exciton (1*s*) and third-class excitons (nd, $n \geq 3$) associated with a unique band edge.

I. INTRODUCTION

Since the classic work of Baldini,[1] there has been an increasing experimental and theoretical interest in excitons in rare-gas atoms and solids.[2,3] The application of synchrotron radiation has made possible optical measurements in a wide spectral region and has further stimulated researchers' attention.

From a theoretical side, two distinct lines of approach have been formulated for an understanding of the exciton spectra in rare-gas solids. The first, more traditional, line (for a thorough review, see Ref. 2) consists in the direct description of crystal excitons. An early attempt in solid argon was made by Knox.[4] Central-cell corrections have been discussed within the pseudopotential formalism[5] and appropriate refinements.[6] The intermediately bound exciton theory,[7,8] besides fostering a renewed interest in the valence-exciton problem, has further stimulated theoretical attention on the inner-shell exciton problem. The second, and more recent, line of approach consists in the description of excitonic spectra in isolated atoms as a preliminary step to considering the more complicated crystal-exciton problem. The formal similarity between atomic excitons and crystal excitons in closed-shell systems has been recognized[9,10] and exploited to relate atomic excitons to crystal excitons in a simple way. The quantum-defect theory for excitons[11] and the nonstructural theory of excitons[12] constitute very meaningful approaches based on simple physical models.

In this paper we examine in a systematic way valence and inner-shell excitons in gaseous and solid argon. The choice of argon is suggested by the following reasons: (i) from an experimental point of view a large amount of data[3] is available for excitons originating from the 3*p*, 3*s*, and 2*p* shells; (ii) from a theoretical point of view conflicting interpretations on the nature of core excitons from the 2*p* shell have been given in the literature.[7,12-14]

The approach we use is based on the envelope-function formalism outlined in previous papers[9,10]; our approach sharply separates the problem of atomic excitons (Sec. II), for which a simple model potential is used, from the problem of crystal excitons (Sec. III), for which no adjustable parameter is introduced. Valence and conduction band shapes are taken into account in the calculations; it is found that valence bandwidth cannot be neglected and actually explains why a 1*s* core exciton is more bound than a 1*s* valence exciton. A new interpretation of the excitonic spectrum originating from the 2*p* shell is provided; our calculations indicate that these excitons correspond to 1*s*, $nd (n \geqslant 3)$ envelope functions and are associated with a unique band-to-band threshold. Section IV contains the conclusions.

II. EXCITONS IN THE ISOLATED ARGON ATOM

The extension of the standard exciton theories[15] to isolated rare-gas atoms has been described elsewhere[9,10] and we recall here only some relevant concepts.

Rare-gas atoms are closed-shell systems and the Hartree-Fock operator, built with ground-state wave functions, has a discrete energy spectrum corresponding to occupied states and a continuous energy spectrum (starting from zero energy) corresponding to virtual states. For simplicity, let us consider excitons originating from an initial atomic state with *s* symmetry. Let $\Psi_{\phi,\Psi_{\vec{k}}}$ be a trial excited state in which the scattering function $\Psi_{\vec{k}}$, corresponding to an impinging plane wave $e^{i\vec{k}\cdot\vec{r}}$ with energy $\hbar^2k^2/2m$, replaces the occupied function ϕ of energy $-E_I$. Atomic excitons near the ionization limit E_I can be described as linear combinations of the type

$$\Psi_{\text{ex}} = \sum_{\vec{k}} A(\vec{k})\Psi_{\phi,\Psi_{\vec{k}}}. \tag{1}$$

The coefficients $A(\vec{k})$ satisfy the standard integral equation

$$\left(\frac{\hbar^2k^2}{2m} + E_I - E\right)A(\vec{k}) + \sum_{\vec{k}'} U(\vec{k},\vec{k}')A(\vec{k}') = 0. \tag{2}$$

The kernel $U(\vec{k},\vec{k}')$ for singlet states is

$$U(\vec{k},\vec{k}') = -\langle\phi\Psi_{\vec{k}}|e^2/r_{12}|\phi\Psi_{\vec{k}'}\rangle + 2\langle\phi\Psi_{\vec{k}}|e^2/r_{12}|\Psi_{\vec{k}'}\phi\rangle. \tag{3}$$

The integral equation (2) can be transformed into a Schrödinger equation for the envelope function

$$F(\vec{r}) = \sum_{\vec{k}} A(\vec{k})e^{i\vec{k}\cdot\vec{r}}.$$

We obtain

$$[-(\hbar^2\nabla^2/2m) + V_h(r) + V_c(r)]F(\vec{r}) = (E - E_I)F(\vec{r}), \tag{4}$$

where $-\nabla^2$ corresponds to the operator k^2 in real space, $V_h(r)$ is the Coulomb potential generated by the hole charge density $e|\phi|^2$, and $V_c(r)$ takes into account atomic central-cell corrections.

As in previous papers[9,10] we do not attempt a first-principles calculation of V_c; rather, we simulate it in the semiempirical form $V_c(r) = A\,S(r - r_0)$, where $S(x)$ is the step function. In numerical calculations the atomic radius r_0 is set equal to 2.34 a.u. and A is left as an adjustable parameter to fit the very accurately known atomic-exciton series. The Coulomb potential $V_h(r)$ is calculated analytically assuming for occupied states Slater-type functions with optimized exponents.[16] For the 3*p* and 3*s* atomic states of argon, we have $\alpha_{3p} = 2.2547$ (in a.u.), $\alpha_{3s} = 2.5856$, and

$$V_h(r) = -e^2/r + e^2\left(\tfrac{2}{45}\alpha^5r^4 + \tfrac{2}{9}\alpha^4r^3 + \tfrac{2}{3}\alpha^3r^2 + \tfrac{4}{3}\alpha^2r + \tfrac{5}{3}\alpha + 1/r\right)e^{-2\alpha r}. \tag{5}$$

For the 2*p* atomic state of argon we have $\alpha_{2p} = 7.0041$, and hence

$$V_h(r) = -e^2/r + e^2\left(\tfrac{1}{3}\alpha^3r^2 + \alpha^2r + \tfrac{3}{2}\alpha + 1/r\right)e^{-2\alpha r}. \tag{6}$$

The eigenfunctions and eigenvalues of Eq. (4) are obtained numerically using standard programs.[17]

In Table I, we report experimental data[18-21] for several exciton series in argon, together with the results of our model calculation and the optimized values of the adjustable parameter A. From Table I, the following remarks can be drawn.

(i) Our model potential provides fairly good agreement with the experimental data for any exciton series. The optimized values of the parameter A (reported in Table I) support the following simple interpretation of the basic equation (4). Besides the kinetic energy and the Coulomb-hole potential, an extra electron with *s* and *p* symmetry feels orthogonalization effects to occupied states, which make A positive. An extra electron with *d* symmetry does not feel orthogonalization effects (in argon there is no occupied *d* level) and the attractive interaction with a polarizable atom may well justify why A is negative in this case.

(ii) The binding energies of excitons (with a given envelope-function symmetry) are practically independent of the degree of localization of the hole left behind. This statement is evident from Table I, where we have included valence-exciton *p* series and *d* series to allow a comparison with the corresponding core-exciton series. By changing $V_h(r)$ in Eq. (4) according to (5) or (6), and keeping V_c constant, we have verified that our proposed model actually leads to eigenvalues almost independent of the hole localization.

Our theory of atomic excitons also allows a simple derivation of selection rules for optical transitions in the dipole approximation. Adapting Elliott's theory[22] to our problem, we first consider the matrix elements $M(\vec{k}) = \langle\Psi_{\vec{k}}|\vec{e}\cdot\vec{r}|\phi\rangle$ between an occupied atomic state ϕ and the scattering state $\Psi_{\vec{k}}$. For small k, $\Psi_{\vec{k}}$ is made up of an *s* wave (with coefficient independent of $\vec{k}$), a *p* wave (with coefficient linear in $\vec{k}$), a *d* wave (with coefficient quadratic in $\vec{k}$), etc. Suppose, for instance, that the atomic state ϕ has *p* symmetry; for small k, $M(\vec{k})$ takes the general form $M(\vec{k}) = C_0 + C_2\vec{k}^2$ and allowed final exciton states have thus either *s* or *d* symmetry (first-class excitons and "third"-class excitons in Elliott's language). Similarly, exciton states originating from *s* occupied states must have *p* symmetry for the envelope function.

Optical transitions from 3*p* or 2*p* shells may lead to excitons with either *s* or *d* symmetry. It is generally agreed[20] that the nodal structure of wave functions makes the *s* series dominant in the former case and the *d* series dominant in the latter.

TABLE I. Experimental transition energies (eV), model calculation results (eV), and optimized values of the semiempirical parameter A (Rydberg) for several valence- and inner-shell exciton series in the argon atom. Transition energies for spin-orbit partner members are not explicity reported, since they can be obtained (with good approximation) by adding the spin orbit splitting of the $3p$ and $2p$ shells, which are 0.178 and 2.148 eV, respectively.

Exciton series	Spectroscopic notations	Envelope-function notations	Experimental transition energies (eV)	Experimental binding energies (eV)	Calculated binding energies (eV)
Valence excitons s series[a]: $A_s=1.34$	$3p_{3/2}\to 4s$	$1s$	11.624	−4.136	−4.134
	$3p_{3/2}\to 5s$	$2s$	14.090	−1.670	−1.706
	$3p_{3/2}\to 6s$	$3s$	14.849	−0.911	−0.929
	$3p_{3/2}\to 7s$	$4s$	15.186	−0.576	−0.584
	$3p_{3/2}\to 8s$	$5s$	15.366	−0.394	−0.400
	edge		15.760		
Valence excitons p series[a]: $A_p=4.20$	$3p_{3/2}\to 4p$	$2p$	13.153	−2.607	−2.604
	$3p_{3/2}\to 5p$	$3p$	14.525	−1.235	−1.234
	$3p_{3/2}\to 6p$	$4p$	15.034	−0.726	−0.727
	$3p_{3/2}\to 7p$	$5p$	15.282	−0.478	−0.479
	edge		15.760		
Valence excitons d series[a]: $A_d=-1.63$	$3p_{3/2}\to 3d$	$3d$	14.153	−1.607	−1.605
	$3p_{3/2}\to 4d$	$4d$	14.859	−0.901	−0.909
	$3p_{3/2}\to 5d$	$5d$	15.190	−0.570	−0.579
	$3p_{3/2}\to 6d$	$6d$	15.350	−0.410	−0.400
	edge		15.760		
Core $3s$ excitons[b]: $A_p=3.60$	$3s\to 4p$	$2p$	26.616	−2.624	−2.624
	$3s\to 5p$	$3p$	27.998	−1.242	−1.245
	$3s\to 6p$	$4p$	28.511	−0.729	−0.730
	$3s\to 7p$	$5p$	28.760	−0.480	−0.480
	edge		29.240		
Core $2p$ excitons[c]: $A_s=1.43, A_d=-1.80$	$2p_{3/2}\to 4s$	$1s$	244.390	−4.238	−4.230
	$2p_{3/2}\to 3d$	$3d$	244.927	−1.701	−1.699
	$2p_{3/2}\to 4d$	$4d$	247.669	−0.959	−0.972
	$2p_{3/2}\to 5d$	$5d$	248.026	−0.602	−0.615
	edge		248.628		

[a] Experimental data from Ref. 18.
[b] Experimental data from Ref. 19.
[c] Experimental data from Ref. 20.

In optical transitions, excitons from the $2p$ shell are thus interpreted as having $1s, 3d, 4d, 5d, \ldots$ symmetry.[20,21] Consider now the modification of atomic exciton energies because of solid-state effects.

III. EXCITONS IN SOLID ARGON

In solid argon, valence-exciton energies and envelope functions are determined by the equation (see Appendix)

$$[E_c(-i\nabla)+E_v(-i\nabla)+V_h(r)+V_c(r)+V_p(r)]\phi(\vec{r}) = (E-E_G)\phi(\vec{r}) , \quad (7)$$

where $E_c(\vec{k})$ is the conduction-band energy (measured from $\vec{k}=0$), $E_v(\vec{k})$ the valence-band energy (measured from $\vec{k}=0$ and of positive sign), $V_p(r)$ the polarization potential, and E_G the energy gap. For core excitons similar equations hold, except that $E_v(\vec{k})$ has to be omitted and E_G has to be replaced by appropriate interband transition energies. We discuss separately polarization effects, energy-band parametrization, and the interpretation of experimental data.

A. Polarization effects

On the basis of simple classical arguments,[23] it has been shown[10] that the electron-hole polarization potential in rare-gas solids takes, for small and large r, the form

$$V_p(r)=\begin{cases} (e^2/R_{ML})(1-1/\epsilon_s) & \text{if } r \ll R_{ML} \\ (e^2/r)(1-1/\epsilon_s) & \text{if } r \gg R_{ML} \end{cases}$$

where R_{ML} is the Mott-Littleton radius for the solid. At the lowest order of approximation, the Mott-Littleton radius is a pure geometrical quantity; in simple fcc lattices $R_{\mathrm{ML}} = \pi a_0/6.3346$, a_0 being the lattice parameter. Both the extended polarizable model of Abarenkov and Antonova[23] and Fowler's treatment[24] of the electron polaron problem lead to the approximate expression

$$V_p(r) = (e^2/r)(1 - 1/\epsilon_s)(1 - e^{-r/R_{ML}}) . \qquad (8)$$

Note that the electron and hole self-energies have not been omitted in Eq. (7); actually they are (tacitly) included in the experimental values of interband edges. In the numerical work we have $\epsilon_s = 1.67$, $a_0 = 10.05$ a.u., $R_{ML} = 4.98$ a.u., and $V_p(0) = 2.19$ eV.

B. Band-structure parametrization

The band structure of solid argon has been calculated by a number of authors[2] and we look here for a simple reasonable parametrization of conduction- and valence-band energies. In the spirit of the Slater-Koster[25] interpolation procedure (see also Ref. 7), we describe the lowest conduction band in the form

$$E_c(\vec{k}) = E_1\left(12 - \sum_{\vec{\tau}_I}^{12} e^{i\vec{k}\cdot\vec{\tau}_I}\right) + E_2\left(6 - \sum_{\vec{\tau}_{II}}^{6} e^{i\vec{k}\cdot\vec{\tau}_{II}}\right), \qquad (9)$$

where $\vec{\tau}_I$ indicates the twelve translation vectors of type $\frac{1}{2}a_0(0,1,1)$ and $\vec{\tau}_{II}$ the six translations vectors of type $a_0(1,0,0)$. The parameters E_1 and E_2 are such to reproduce the calculated[26] values 2.58 and 3.16 eV at X and L points of the Brillouin zone. At $\vec{k} = 0$ the resulting effective mass $m_c^* = 0.51 m_e$ is in fair agreement with other values given in the literature.[2]

The parametrization of the valence band poses a more subtle problem because of threefold degeneracy of the atomic p levels. Following Slater and Koster,[25] we express in terms of independent parameters the matrix elements $H_{ij}(i,j = x,y,z)$ of the crystal Hamiltonian between Bloch sums formed with p_x, p_y, and p_z orbitals, and take into account only the nearest-neighbor interactions. The arithmetic average of the three valence-band eigenvalues at any given $\vec{k}$ is $\frac{1}{3}\mathrm{Tr}H_{ij}$; we easily obtain

$$E_v(\vec{k}) = \frac{\Delta_v}{16}\left(12 - \sum_{\vec{\tau}_I}^{12} e^{i\vec{k}\cdot\vec{\tau}_I}\right), \qquad (10)$$

where Δ_v is the valence bandwidth. From experiments[27] we set $\Delta_v = 1.7$ eV. At $\vec{k} = 0$, parametrization (10) gives $m_v^* = 1.27 m_e$ for the averaged effective mass. Whenever necessary, the spherical average of (9) or (10) is obtained by replacing the exponentials with zero-order spherical Bessel functions.

C. Details of calculations

We have now all the ingredients for going back to Eq. (7), whose solution appears difficult because of the complicated nature of the "band kinetic operator" $E_c(-i\nabla) + E_v(-i\nabla)$. However, after several attempts: variational methods, conversion to a matrix equation, simulation of an r-dependent effective mass,[5] and replacement of the kinetic energy operator by the symmetrical form $\frac{1}{4}[1/m(r)]p^2 + \frac{1}{4}p^2[1/m(r)]$, we have found a rather economical (and unexpectedly accurate) approach.

We now replace in Eq. (7) the complicated operator $E_c(-i\nabla) + E_v(-i\nabla)$ by a "traditional" kinetic operator $-\hbar^2\nabla^2/2m^*$ with a fixed value of m^*, and solve the resulting equation almost exactly using standard programs.[17] We then consider the quantity

$$\Delta E = \int \phi^*(\vec{r})\left[E_c(-i\nabla) + E_v(-i\nabla) - \left(-\frac{\hbar^2\nabla^2}{2m^*}\right)\right]\phi(\vec{r})\,d\vec{r} \qquad (11a)$$

$$= \int |A(\vec{k})|^2\left[E_c(\vec{k}) + E_v(\vec{k}) - \frac{\hbar^2 k^2}{2m^*}\right]d\vec{k}, \qquad (11b)$$

where $A(\vec{k})$ indicates the Fourier transform of $\phi(\vec{r})$, and we numerically evaluate (11b). We find that the first-order eigenvalues $E + \Delta E$ are rather insensitive to the chosen value of m^*, though E and ΔE separately depend sensitively on it. (See Table II for an illustration). The final eigenvalues reported in Table III are those for which expression (11b) vanishes.

For sake of completeness, we have also verified that more realistic expressions of $E_c(\vec{k})$ outside the first Brillouin zone produce minor effects even on the lowest-lying excitons. This confirms the point of view of Altarelli *et al.*[7] that, among conduction states, only the lowest-lying band is important for the description of excitons in solid argon.

D. Interpretation of experimental data

In Table III, besides our computed exciton energies, we have also reported for convenience experimental transition energies.[28-30] For valence excitons and core excitons originating from the $3s$ level, no problem exists in the interpretation of the experimental data. In our calculations the binding energy of higher exciton members is insensitive to both the detailed band-structure shape (the dominant role being played by the effective mass at Γ) and the interpolation formula (8) [for large r the polarization potential being $e^2(1 - 1/$

TABLE II. Illustrative example of the computation of the binding energy of the 1*s* valence exciton in solid argon. Energies are in eV and m^* in electron mass units. E_{1s} is the 1*s* eigenvalue of Eq. (7) with $E_c(-i\nabla)+E_v(-i\nabla)$ replaced by $-\hbar^2\nabla^2/2m^*$. ΔE is calculated from Eq. (11b). The corrected eigenvalue of −1.869 is the final energy reported in Table III.

m^*	0.40	0.46	0.50	0.60	0.70	0.80	0.90	1.00
E_{1s}	−1.716	−1.871	−1.965	−2.171	−2.345	−2.496	−2.629	−2.746
ΔE	−0.116	0.002	0.077	0.270	0.366	0.508	0.638	0.752
$E_{1s}+\Delta E$	−1.832	−1.869	−1.888	−1.901	−1.979	−1.988	−1.991	−1.994

$\epsilon_s)(1/r)]$. We can thus estimate the energy position of the interband edges by adding calculated binding energies for shallow excitons to experimental transition energies. In this way we obtain an energy gap of ≈14.08 eV and the onset of band-to-band transitions from the 3*s* atomic level at ≈28.40 eV. In the case of core excitons from 2*p* levels, the situation in the literature is more uncertain and very different interpretations[7,12,13,14] of experimental data[30] have been given.

From Table III we see that the 1*s* core exciton is bound much more than the 1*s* valence exciton, the valence bandwidth being responsible of this change. The binding energies of the 3*d*, 4*d*, and 5*d* excitons are instead very small (−0.31, −0.16, and −0.10 eV). We ascribe the absorption bands[30] *A* and *B* peaked at 245.2 and 247.85 eV (optical experiments[30] were performed with a 0.3-eV slit width) to 1*s* and $nd(n\geq 3)$ excitons, respectively. Since in the isolated atom the generalized oscillator strength density[20] is a maximum at the 5*d* exciton energy, in the solid we also associate the peak in *B* to the 5*d* exciton. (The assignment of this peak to the 5*d* or the 3*d*, 4*d*, ... members is almost irrelevant because of the smallness of *d*-exciton binding energies). The absorption bands[30] *A′* and *B′* at 247.36 and 250.25 eV are interpreted, as usual, as spin-orbit partners of *A* and *B*. Having realized the importance of "third-class excitons" in the more simple atomic problem (Sec. II), we form the plausible hypothesis that this role is preserved upon passing to the solid. The present interpretation is quite different from those given in the literature.[7,12-14] However, with respect to the interpretation of Altarelli *et al.*,[7] we share the point of view that, because of valence

TABLE III. Computed binding energies (eV) and experimental transition energies for valence and inner-shell excitons in solid argon.

Exciton series	Envelope-function notations	Experimental transition energies (eV)	Expt. transition energies referred to the estimated edge (eV)	Calculated binding energies (eV)
Valence excitons[a]	1*s*	12.06	−2.02	−1.869
	2*s*	13.57	−0.51	−0.470
	3*s*	13.89	−0.19	−0.186
	4*s*	13.97	−0.11	−0.106
	5*s*			−0.068
	Estimated edge	14.08		
Core 3*s* excitons[b]	2*p*	27.52	−0.88	−1.019
	3*p*	28.00	−0.40	−0.375
	4*p*			−0.164
	5*p*			−0.104
	Estimated edge	28.40		
Core 2*p* excitons[c]	1*s*	245.2	−2.75	−2.435
	3*d*			−0.308
	4*d*			−0.159
	5*d*	247.85	−0.10	−0.102
	Estimated edge	247.95		

[a] Experimental data from Ref. 28.
[b] Experimental data from Ref. 29.
[c] Experimental data from Ref. 30.

bandwidth, the 1s core exciton is more bound than the 1s valence exciton is; furthermore, the importance of the d excitons[7,12] is confirmed.

Our interpretation of the experimental data is also corroborated by the comparison of energy thresholds in gaseous and solid argon. The ionization energies of the argon atom, reported in Table I, are $I_{3p} = 15.76$ eV, $I_{3s} = 29.24$ eV, and $I_{2p} = 248.63$ eV. In the solid our estimated onsets of band-to-band transitions (Table III) are $E_{3p} = 14.08$ eV, $E_{3s} = 28.40$ eV, and $E_{2p} = 247.95$ eV. We can make the following remarks.

(i) The ionization energies in the atom are systematically higher than the corresponding energy thresholds in the crystal. (ii) The differences between the energy edges in the atom and the solid, when corrected for the occupied band half-width, are almost constant; a justification of this is obtained by extending to deep levels the considerations of Raz and Jortner.[31] Assuming[27] the half width of the valence band$\approx$0.85 eV, deeper valence and core bands infinitely narrow, we obtain, in fact, $I_{3p} - E_{3p} - \frac{1}{2}\Delta_v = 0.83$ eV, $I_{3s} - E_{3s} = 0.84$ eV, and $I_{2p} - E_{2p} = 0.68$ eV.

Before concluding this section, we note that our calculations of $3p_{3/2} \to ns$ exciton binding energies use the experimental valence bandwidth ($\approx$1.7 eV, Ref. 27), which refers to both valence-band spin-orbit partners. In principle one should use rather the valence bandwidth computed in the nonrelativistic limit; such a bandwidth should approximately equal 1.5 eV, which is the experimental bandwidth minus the atomic spin-orbit splitting ($\approx$0.18 eV, Ref. 18). However, in the case of argon, the use of one or the other of the above-mentioned values makes little difference even on 1s valence excitons [if $\Delta_v = 1.7$ eV, $E_{1s} = -1.869$ eV and $E_{2s} = -0.470$ eV (see Table III); if $\Delta_v = 1.5$ eV, $E_{1s} = -1.915$ eV and $E_{2s} = -0.485$ eV].

IV. CONCLUSIONS

In this paper we have discussed atomic excitons in closed-shell atoms, starting from the integral exciton equation of solid-state theory. The difficult to solve first-principle equations have been simplified by exploiting atomic spectroscopy data. Solid-state effects, which include band-structure and electron-hole screening, are then taken into account with appropriate simplifications. A satisfactory interpretation of similarities and differences between exciton series in solid argon and between the solid and the gas is achieved. The treatment of the present paper should allow a better understanding of excitons in the other rare-as solids and in the class of crystals made up of osed-shell units.

APPENDIX

The aim of this Appendix is to derive Eq. (7), which exploits the results pertaining to atomic excitons in argon (Sec. II) to simplify the difficult to solve first-principle equations for excitons in the solid.

We start from the standard integral equations for direct (singlet) excitons in a generic semiconductor or insulator,[15]

$$[E_c(\vec{k}) - E_v(\vec{k}) - E]A_{cv}(\vec{k}) + \sum_{c'v'} \sum_{\vec{k}'}^{BZ} U_{cv;c'v'}(\vec{k},\vec{k}')A_{c'v'}(\vec{k}') = 0\,, \quad (12)$$

where $E_v(\vec{k})$, $\Psi_{v\vec{k}}$ indicate energies and wave functions of occupied states (valence or core states), $E_c(\vec{k})$, $\Psi_{c\vec{k}}$ indicate energies and wave functions of conduction states, $\vec{k}$ and $\vec{k}'$ are confined to the first Brillouin zone (BZ), and the kernel U is defined as

$$U_{cv;c'v'}(\vec{k},\vec{k}') = -\langle \Psi_{v'\vec{k}'}\Psi_{c\vec{k}} | e^2/r_{12} | \Psi_{v\vec{k}}\Psi_{c'\vec{k}'} \rangle + 2\langle \Psi_{v'\vec{k}'}\Psi_{c\vec{k}} | e^2/r_{12} | \Psi_{c'\vec{k}'}\Psi_{v\vec{k}} \rangle . \quad (13)$$

In principle the system of integral equations (12) contains all couples of occupied and empty bands. For simplicity we consider the specific case of excitons originating from an s-like occupied band; since in solid rare gases occupied bands originating from different shells are well separated in energy, the sum over v' in Eq. (12) becomes inessential. We can also formally drop the sum over c' in (12), letting $\vec{k}$ and $\vec{k}'$ run on the whole reciprocal lattice (which corresponds to describing all conduction bands in the extended zone scheme) and rewrite Eq. (12) in the form

$$[E_c(\vec{k}) - E_v(\vec{k}) - E]A(\vec{k}) + \sum_{\vec{k}'} U(\vec{k},\vec{k}')A(\vec{k}') = 0\,, \quad (14)$$

where

$$U(\vec{k},\vec{k}') = -\langle \Psi_{v\vec{k}'}\Psi_{c\vec{k}} | e^2/r_{12} | \Psi_{v\vec{k}}\Psi_{c\vec{k}'} \rangle + 2\langle \Psi_{v\vec{k}'}\Psi_{c\vec{k}} | e^2/r_{12} | \Psi_{c\vec{k}'}\Psi_{v\vec{k}} \rangle , \quad (15)$$

and $\vec{k}, \vec{k}'$ now run over the whole reciprocal lattice.

It is convenient to describe the wave functions $\Psi_{v\vec{k}}$ by the Block sums

$$\Psi_{v\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{\tau}_n} e^{i\vec{k}\cdot\vec{\tau}_n} a_v(\vec{r} - \vec{\tau}_n)\,, \quad (16)$$

where a_v is the Wannier function of the occupied band under consideration. In the closed-shell rare-gas solids, the Wannier functions a_v of the occupied bands do not differ appreciably from the atomic functions ϕ; furthermore, the occupied atomic functions ϕ are reasonably well localized with respect to the nearest-neighbor distance. Using these facts and substituting (16) into (15), we obtain approximately,

$$U(\vec{k},\vec{k}') = -\langle \phi \Psi_{c\vec{k}} | e^2/r_{12} | \phi \Psi_{c\vec{k}'} \rangle + 2\langle \phi \Psi_{c\vec{k}} | e^2/r_{12} | \Psi_{c\vec{k}'} \phi \rangle . \qquad (17)$$

In rare-gas solids the conduction wave functions $\Psi_{c\vec{k}}$ (with $\vec{k}$ in the extended zone scheme) are expected to be reasonably near the scattering atomic functions $\Psi_{\vec{k}}$ of Sec. II. Thus the replacement of the kernel for crystal excitons with the kernel for atomic excitons made in Eq. (7) is justified from a formal point of view. From a heuristic point of view, we notice that Eq. (7) is *exact* anyway if the crystal excitons are either very well localized or very well delocalized with respect to the unit cell. The considerations of this Appendix are applicable whenever crystal excitons occur between reasonably narrow occupied bands and free-electron-like conduction bands, which is the typical situation of most crystals made up of closed-shell units.

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