

Electronic Band Structure and Wannier Exciton States in Solid Krypton*†

W. BEALL FOWLER

University of Rochester, Rochester, New York

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The electronic band structure of solid krypton has been calculated by a combined tight-binding and orthogonalized plane wave approach first introduced by Knox and Bassani. The crystal potential, constructed as a sum of quasiatomic potentials, contains an exchange potential which has been made to approximate closely the crystal Slater exchange potential. Spin-orbit splittings have been computed, and effective masses have been obtained at points of high symmetry in the Brillouin zone. The smallest computed gap between valence and conduction bands is "direct," is located at $\Gamma(\mathbf{k}=0)$, and has a magnitude of 11.3 ± 1.0 eV, in agreement with the direct gap of 11.8 eV inferred by Baldini on the basis of optical absorption data. Computed Wannier exciton absorption lines at Γ are also in agreement with Baldini's results.

I. INTRODUCTION

THE solid rare gases have for many years been of physical interest,¹ both for their intrinsic properties and for the insight into the properties of other solids which their study might yield. Recently attention has been focused upon their electronic characteristics. Foner *et al.*² have measured the magnetic properties of impurities in solid rare gases; this problem has been studied theoretically by Adrian and by Smith.³ Optical properties have also been measured and several relevant calculations made.

In 1958, Knox⁴ calculated the properties of Frenkel excitons^{5,6} in solid argon, and more recently the electronic band structure of argon has been calculated by Knox and Bassani⁷ and by Mattheiss⁸ (who used the APW method). Absorption line shapes have been considered theoretically by Meijer and by Gold and Knox.⁹ Early work on absorption spectra of the rare gas solids¹⁰ was followed by that of Baldini,¹¹ who, by using ingenious techniques, was able to obtain spectra over a fairly large energy range in argon, krypton, and xenon. Baldini's surprising success in fitting certain observed lines in krypton and xenon by the model of hydrogenic

Wannier excitons^{6,12,13} indicated that effective-mass methods, which have been of great usefulness in the study of semiconductors, might be relevant in calculating properties of the rare gas solids.

As a first step in the use of such methods, we have calculated the electronic band structure of krypton, including the spin-orbit interaction, and have computed effective electron and hole masses. Properties of hydrogenic Wannier excitons at $\Gamma(\mathbf{k}=0)$ have been calculated, and our results have been compared with Baldini's data.

We have used the tight-binding method^{7,14} to calculate valence bands, and the full orthogonalized plane wave (OPW) method to calculate conduction bands. Although the OPW method, introduced by Herring¹⁵ around 1940, has been used with considerable success in computing the band structure of semiconductors,¹⁶ it had not until recently been employed for larger band-gap materials such as ionic crystals and rare gas solids. This is probably due to the fact that the valence bands in such substances are considered to be "tightly bound," and that an expansion of such valence band wave functions in OPW's would probably not converge rapidly. On the other hand, the valence bands are expected to have some structure, and it would not be accurate to treat them as flat core bands. Knox and Bassani,⁷ therefore, used the tight-binding method to calculate the valence bands in solid argon and then used a perturbation approximation¹⁷ to the OPW method to calculate conduction bands. Our procedure is similar, except that we have used the full OPW method to compute conduction bands.

As a parameter in the calculation we have used a lattice constant $a=10.75a_0$ (Bohr radii) for fcc solid

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† Based on a thesis submitted by the author in partial fulfillment of the requirements for the Ph.D. degree at the University of Rochester.

¹ E. R. Dobbs and G. O. Jones, Rept. Progr. Phys. **20**, 516 (1957).

² S. N. Foner, E. L. Cochran, V. A. Bowers, and C. K. Jen, J. Chem. Phys. **32**, 963 (1960).

³ F. Adrian, J. Chem. Phys. **32**, 972 (1960); D. Y. Smith, Phys. Rev. **131**, 2056 (1963).

⁴ R. S. Knox, J. Phys. Chem. Solids **9**, 265 (1959).

⁵ J. Frenkel, Phys. Rev. **37**, 17 and 1276 (1931).

⁶ R. S. Knox, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, to be published), Suppl. 5.

⁷ R. S. Knox and F. Bassani, Phys. Rev. **124**, 652 (1961).

⁸ L. F. Mattheiss, Quarterly Progress Report No. 46, 1962, Solid-State and Molecular Theory Group, MIT, Cambridge, Massachusetts (unpublished).

⁹ P. H. E. Meijer, J. Chem. Phys. **34**, 2078 (1961); A. Gold and R. S. Knox, *ibid.* **36**, 2805 (1962).

¹⁰ O. Schnepf and K. Dressler, J. Chem. Phys. **33**, 49 (1960); J. R. Nelson and P. L. Hartman, Bull. Am. Phys. Soc. **4**, 371 (1959).

¹¹ G. Baldini, Phys. Rev. **128**, 1562 (1962).

¹² G. H. Wannier, Phys. Rev. **52**, 191 (1937).

¹³ R. J. Elliott, Phys. Rev. **108**, 1384 (1957); G. Dresselhaus, J. Phys. Chem. Solids **1**, 14 (1956).

¹⁴ F. Bloch, Z. Physik **52**, 555 (1928).

¹⁵ C. Herring, Phys. Rev. **57**, 1169 (1940).

¹⁶ F. Herman, Phys. Rev. **93**, 1214 (1954); F. Bassani and M. Yoshimine, *ibid.* **130**, 20 (1963); R. C. Casella, *ibid.* **109**, 54 (1958).

¹⁷ F. Bassani and V. Celli, Nuovo Cimento **11**, 805 (1959); Studia Ghisleriana **2**, 157 (1959); J. Phys. Chem. Solids **20**, 64 (1961).

krypton, which corresponds to the density at about 50°K.¹⁸ We have also employed Watson and Freeman's¹⁹ Hartree-Fock atomic functions for krypton. Numerical work was largely performed on the IBM-7070 digital computer at the University of Rochester, although several calculations were also performed on the IBM-704 computer at Argonne National Laboratory. For details of the calculation not presented here the reader is referred to the author's thesis.²⁰

In Sec. II we discuss the choice of a crystal potential. The valence bands are calculated in Sec. III; in Sec. IV the spin-orbit interaction is added to the valence bands; and in Sec. V the conduction bands are considered. In Sec. VI effective masses are calculated, and in Sec. VII the preceding results are applied to the Wannier exciton model and comparisons are made with Baldini's experimental results.

II. THE CRYSTAL POTENTIAL

The one-electron crystal potential may be written as a sum of quasiautomic potentials,

$$V(\mathbf{r}) = \sum_{\nu} V_a(\mathbf{r} - \mathbf{R}_{\nu}), \quad (1)$$

where \mathbf{R}_{ν} represents the position of the ν th lattice site. The Coulomb part of $V(\mathbf{r})$ is chosen to be a simple sum of Coulomb potentials of free krypton atoms; this is a reasonably good approximation, since the Coulomb potential is a linear function of the charge density, and the overlap of charge densities of neighboring atoms is small.

Slater²¹ has derived an approximate exchange potential based only upon charge densities:

$$V_{\text{ex}}(\mathbf{r}) = a\rho^{1/3}, \quad (2)$$

where ρ is the charge density and a is equal to

$$-6[3/8\pi]^{1/3}$$

when V_{ex} is in Ry. In some previous calculations this has been approximated for the crystal as

$$V_{\text{ex}}(\mathbf{r}) \approx a \sum_{\nu} [\rho(\mathbf{r} - \mathbf{R}_{\nu})]^{1/3}, \quad (3)$$

whereas the actual value would be

$$V_{\text{ex}}(\mathbf{r}) = a[\sum_{\nu} \rho(\mathbf{r} - \mathbf{R}_{\nu})]^{1/3}. \quad (4)$$

Investigation of this approximation shows that the use of Eq. (3) leads to a potential which is fairly close to that of Eq. (4) for small $|\mathbf{r} - \mathbf{R}_{\nu}|$, but which is too large for larger $|\mathbf{r} - \mathbf{R}_{\nu}|$. This approximation was used by Knox and Bassani⁷ in their argon-band-structure

calculation, with reasonable results (although their predicted band gap was ≈ 1.8 eV too small). However, the use of a Slater exchange potential, at least in the approximation of Eq. (3), in an ionic crystal (AgCl) leads to unreasonable results.²²

It is not simple to make an analytic correspondence between $\sum_{\nu} V_a^{\text{ex}}(\mathbf{r} - \mathbf{R}_{\nu})$ and Eq. (4). What has been done in the present calculation is to construct a potential (as a sum of quasiautomic potentials) which is equal to a sum of atomic Slater potentials [Eq. (3)] for $|\mathbf{r} - \mathbf{R}_{\nu}| \leq 2.0a_0$, a somewhat arbitrary number. For larger $|\mathbf{r} - \mathbf{R}_{\nu}|$ the potential is made smaller than $a \sum_{\nu} \rho_{\nu}^{1/3}$ by multiplying the atomic Slater potential by an exponential factor. The damping length is determined by requiring that the exchange potential due to nearest neighbor atoms at their midpoint be equal to that given by Eq. (4). This procedure, admittedly crude, nevertheless yields a potential which more closely approximates the potential of Eq. (4) than does that of Eq. (3).

This procedure has nothing to do with many-body effects, such as those considered by Robinson, Bassani, Knox, and Schrieffer²³ (RBKS) or by Bassani, Robinson, Goodman, and Schrieffer.²⁴ In the RBKS approach an exchange potential is derived as a function of an effective dielectric constant. The relationship between this dielectric constant and a given physical dielectric constant has not been firmly established, but if it is assumed in our case that the dielectric constant is that of krypton ($\epsilon = 1.80$), then RBKS screening of the Slater potential is small.²³ In Fig. 1 we have plotted $rV_a^{\text{ex}}(r)$ for the atomic Slater potential, our "corrected" Slater potential, and an infinite-dielectric-constant RBKS potential (which probably is not pertinent to the case of krypton).

III. THE VALENCE BANDS

The one-electron Hamiltonian is

$$\mathcal{H} = p^2/2m + \sum_{\nu} V_a(\mathbf{r} - \mathbf{R}_{\nu}) \quad (5)$$

and the eigenfunction of \mathcal{H} in a tight-binding representation is

$$\phi_i^{\alpha}(\mathbf{k}, \mathbf{r}) = \sum_n a_{in}^{\alpha} (NO^{n,\alpha})^{-1/2} \sum_{\nu} e^{i\mathbf{k} \cdot \mathbf{R}_{\nu}} v_n^{\alpha}(\mathbf{r} - \mathbf{R}_{\nu}), \quad (6)$$

where

$$v_n^{\alpha}(\mathbf{r} - \mathbf{R}_{\nu}) = \sum_m c_{nm}^{\alpha} u_{nm}(\mathbf{r} - \mathbf{R}_{\nu}). \quad (7)$$

The quantities $u_{nm}(\mathbf{r} - \mathbf{R}_{\nu})$ are atomic wave functions centered at \mathbf{R}_{ν} , and c_{nm}^{α} are constants which choose linear combinations of a set of degenerate u_{nm} which

²² R. S. Knox, F. Bassani, and W. Beall Fowler, *Suppl. J. Phys. Soc. Japan* (to be published).

²³ J. E. Robinson, F. Bassani, R. S. Knox, and J. R. Schrieffer, *Phys. Rev. Letters* **9**, 521 (1962).

²⁴ F. Bassani, J. Robinson, B. Goodman, and J. R. Schrieffer, *Phys. Rev.* **127**, 1969 (1962).

¹⁸ B. F. Figgins and B. L. Smith, *Phil. Mag.* **5**, 186 (1960).

¹⁹ R. E. Watson and A. J. Freeman, *Phys. Rev.* **124**, 1117 (1961).

²⁰ W. Beall Fowler, thesis, University of Rochester, 1963 (unpublished).

²¹ J. C. Slater, *Phys. Rev.* **81**, 385 (1951).

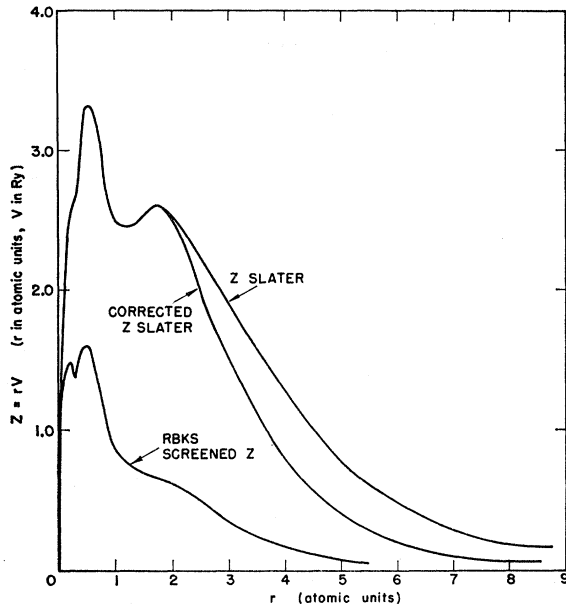


FIG. 1. Several approximate one-electron exchange potentials for krypton (see text).

transform according to the α irreducible representation of the group of \mathbf{k} .²⁵ $O^{n,\alpha}$ is defined by

$$O^{n,\alpha} = \sum_{\nu} e^{i\mathbf{k}\cdot\mathbf{R}_{\nu}} \langle v_n^{\alpha}(\mathbf{r}) | v_n^{\alpha}(\mathbf{r}-\mathbf{R}_{\nu}) \rangle \quad (8)$$

and N is the number of lattice sites. The quantities a_{in}^{α} are determined by solution of the secular equation for E .

The energies are given by the solutions of $\det M = 0$, where M is a matrix whose elements are

$$M_{nn'} = (O^{n,\alpha} O^{n',\alpha})^{-1/2} \sum_{\nu} e^{i\mathbf{k}\cdot\mathbf{R}_{\nu}} \times \langle v_n^{\alpha}(\mathbf{r}) | \mathcal{H} - E | v_n^{\alpha}(\mathbf{r}-\mathbf{R}_{\nu}) \rangle. \quad (9)$$

In practice, one does not include an infinite number of atomic-like states in the matrix M , and, in fact, we have considered mixing only between $4s$ and $4p$ states; even this involved an energy change of only order 1%.

The integrals in Eq. (9) are of one-, two-, and three-center types. To evaluate certain of the one- and two-center integrals, we made the approximation

$$[\mathcal{H}^2/2m + V_a(\mathbf{r}-\mathbf{R}_{\nu})] u_{nm}(\mathbf{r}-\mathbf{R}_{\nu}) = \epsilon_{nm}^{\alpha} u_{nm}(\mathbf{r}-\mathbf{R}_{\nu}), \quad (10)$$

where

$$\epsilon_{nm}^{\alpha} = \epsilon_{nm}^{\text{atomic}} + \langle u_{nm}(\mathbf{r}) | V_a(\mathbf{r}) - V_{\text{atomic}}(\mathbf{r}) | u_{nm}(\mathbf{r}) \rangle; \quad (11)$$

we recall that our one-electron functions $u_{nm}(\mathbf{r}-\mathbf{R}_{\nu})$ are eigenfunctions of $\mathcal{H}^2/2m + V_{\text{atomic}}(\mathbf{r}-\mathbf{R}_{\nu})$. This

²⁵ L. P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. **50**, 58 (1936).

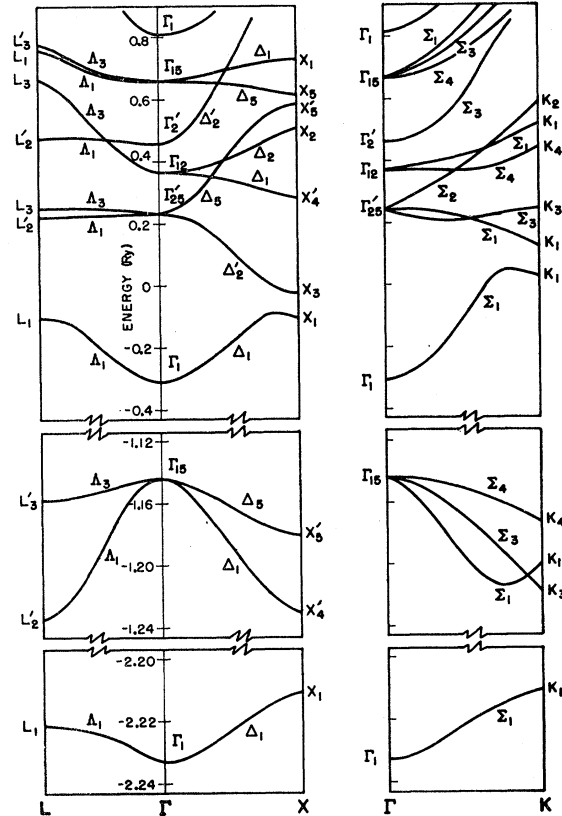


FIG. 2. Krypton band structure (without spin-orbit coupling). Note the several changes in scale between $4s$ and $4p$ valence bands and conduction bands. Notation is that of Bouckaert, Smoluchowski, and Wigner (Ref. 25).

approach is reasonably accurate if the difference between $V_a(\mathbf{r})$ and $V_{\text{atomic}}(\mathbf{r})$ is small. It ignores the fact that Hartree-Fock functions are not eigenfunctions of the quasiatomic potential, but it does account through first-order perturbation theory for the shift in energy due to use of this potential.

We have neglected all three-center terms. They are difficult to calculate, and in the case of krypton they can be shown to be at least an order of magnitude smaller than corresponding two-center integrals.

Two-center terms were calculated for nearest and next-nearest neighbors. The latter turned out to give negligible contributions to the energy. Standard techniques were used in writing²⁶ and evaluating²⁷ two-center integrals.

Computed valence band energies are shown in the two lowest sets of bands of Fig. 2, for the corrected Slater exchange potential. We also have calculated the energies at Γ , using atomic Slater and infinite-dielectric-constant RBKS potentials. We obtained for the Slater potential $E(\Gamma_1) = -2.47$ and $E(\Gamma_{15}) = -1.43$ Ry, for the RBKS potential $E(\Gamma_1) = -0.85$, $E(\Gamma_{15}) = +0.02$ Ry.

²⁶ J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

²⁷ P. O. Löwdin, Suppl. J. Appl. Phys. **33**, 251 (1962).

Results for the RBKS potential are not very accurate, however; this potential is so much different from the atomic exchange potential that the first-order perturbation technique for calculating ϵ^α [Eq. (11)] is obviously not valid.

We see that the valence bands are really rather flat, especially the 4s band, and the assumption of flat core bands is certainly well justified. We estimate that the position of the Γ_{15} valence state is computationally accurate to within 0.01 Ry, the width of the 4p valence band is accurate to within 0.01 Ry, and the position of the 4s valence band is accurate to within 0.05 Ry.

IV. SPIN-ORBIT INTERACTION IN THE VALENCE BANDS

The usual one-electron spin-orbit coupling term is

$$H_{s.o.} = (\hbar/4m^2c^2)\boldsymbol{\sigma} \cdot (\nabla V \times \mathbf{p}), \quad (12)$$

where $\boldsymbol{\sigma}$ represents the Pauli matrices, V the potential, and \mathbf{p} the momentum. This result may be obtained by writing a many-electron Dirac-type equation, using the one-electron approximation and the variational method to obtain a Hartree-Fock-like equation,²⁸ replacing Coulomb and exchange terms by an effective potential, and going to the low-energy limit.²⁹ From a theoretical point of view, it is not clear that the effective potential V should be the same as that used previously, or how, in particular, exchange should be treated.³⁰ If we use the same effective potential we find (a) the contribution of the exchange potential is only a few percent that of the Coulomb potential, and (b) for the Coulomb potential, ∇V is only large very near the nuclei, and thus all many-centered terms are negligible. The effective spin-orbit interaction is, thus,

$$H_{s.o.}^{\text{eff}} = \frac{\hbar}{4m^2c^2} \frac{1}{r} \frac{dV_a(r)}{dr} \boldsymbol{\sigma} \cdot \mathbf{L}, \quad (13)$$

where \mathbf{L} is equal to $\mathbf{r} \times \mathbf{p}$.

The procedure for incorporating $H_{s.o.}^{\text{eff}}$ into the tight-binding calculation is straightforward. One takes space- and spin-eigenfunctions of the tight-binding calculation without spin-orbit interaction, forms linear combinations of these which transform according to a particular irreducible representation of the crystal double group^{31,32} and includes $H_{s.o.}^{\text{eff}}$ in the energy matrix. This is similar to the procedure used in atomic physics, when one takes eigenstates of l , m_l , s , m_s , and forms linear combinations which are eigenstates

²⁸ B. Swirls, Proc. Roy. Soc. (London) **A152**, 625 (1935); **A157**, 680 (1936).

²⁹ J. Callaway, R. D. Woods, and V. Sirounian, Phys. Rev. **107**, 934 (1957).

³⁰ However, see M. Blume and R. E. Watson, Proc. Roy. Soc. (London) **A270**, 127 (1962) for a discussion of the role of exchange.

³¹ R. J. Elliott, Phys. Rev. **96**, 266 and 280 (1954).

³² G. F. Koster and H. Statz, Quarterly Progress Report No. 39, 1961, Solid State and Molecular Theory Group, MIT, Cambridge, Massachusetts (unpublished).

of J and J_z . The relevant group theory has been treated by Koster and Statz,³² and we use their results.

If we redefine our basic atomic linear combinations as follows:

$$v_n^\alpha(\mathbf{r} - \mathbf{R}_\nu, \boldsymbol{\sigma}) \equiv \sum_{m_l} \sum_{m_s} c_{nm_l m_s}^\alpha u_{nm_l}(\mathbf{r} - \mathbf{R}_\nu) \chi(\boldsymbol{\sigma}, m_s), \quad (14)$$

the general tight-binding matrix element remains the same in form, with $H_{s.o.}^{\text{eff}}$ included in the Hamiltonian. The only changes in the matrix elements will be one-center terms involving $H_{s.o.}^{\text{eff}}$. These will result in the removal of degeneracies and the mixing of hitherto orthogonal states. For example (now in the notation of the crystal double group),

$$E(\Gamma_6^-) = E(\Gamma_{15}) + \frac{\langle v_p(\Gamma_6^-; \mathbf{r}, \boldsymbol{\sigma}) | H_{s.o.}^{\text{eff}} | v_p(\Gamma_6^-; \mathbf{r}, \boldsymbol{\sigma}) \rangle}{O(p, \Gamma_{15})}. \quad (15)$$

We have computed the relevant matrix elements and thus the energies. The results are shown in Fig. 3. We see that splitting is fairly pronounced. Although the 4p-like bands still overlap somewhat, in xenon, the next rare gas in the periodic system, the highest valence bands might not overlap.

V. THE CONDUCTION BANDS

The full orthogonalized-plane-wave (OPW) method^{15,16} was used to calculate conduction band energies. The basis set associated with this method is given by

$$\varphi_p^\alpha = S_p^\alpha - \sum_i \langle \phi_i^\alpha, S_p^\alpha \rangle \phi_i^\alpha, \quad (16)$$

where ϕ_i^α is a core or valence eigenfunction and S_p^α is a particular linear combination of degenerate plane waves, i.e.,

$$S_p^\alpha = (N\Omega)^{-1/2} \sum_i b_{pj}^\alpha e^{i(\mathbf{k} + \mathbf{h}_j) \cdot \mathbf{r}}. \quad (17)$$

The quantities b_{pj}^α are chosen so that S_p^α transforms according to the α irreducible representation of the group of \mathbf{k} .²⁵ N represents the number of unit cells of volume Ω . The wave function will be

$$\psi_q^\alpha(\mathbf{k}, \mathbf{r}) = \sum_p d_{q,p}^\alpha \varphi_p^\alpha. \quad (18)$$

The conduction band wave functions and energies are solutions of the equation $\det M = 0$, where the matrix M has elements

$$M_{pp'} = \langle S_{p'}^\alpha | p^2/2m + V(\mathbf{r}) | S_p^\alpha \rangle - \sum_i \langle S_{p'}^\alpha, \phi_i^\alpha \rangle \times \langle \phi_i^\alpha, S_p^\alpha \rangle E_i^\alpha - E[\delta_{pp'} - \sum_i \langle S_{p'}^\alpha, \phi_i^\alpha \rangle \langle \phi_i^\alpha, S_p^\alpha \rangle]. \quad (19)$$

Here E_i^α is the core or valence eigenvalue of the one-electron crystal potential.

Evaluation of the various terms in $M_{pp'}$ has been described in several places in the literature.^{7,16,33} The potential $V(\mathbf{r})$ is expanded in Fourier series;

$$V(\mathbf{r}) = \sum_{\mathbf{K}} v(\mathbf{K}) e^{i\mathbf{K}\cdot\mathbf{r}}, \quad (20)$$

The Fourier coefficients $v(\mathbf{K})$ may be computed and this part of $M_{pp'}$ evaluated. $v(\mathbf{K})$ is given by

$$v(\mathbf{K}) = 4\pi(K\Omega)^{-1} \int_0^\infty r \sin(Kr) V_a(r) dr; \quad (21)$$

$v(0)$ is given by

$$v(0) = 4\pi\Omega^{-1} \int_0^\infty r^2 V_a(r) dr. \quad (22)$$

Evaluation of $v(0)$ is subject to error, since $v(0)$ depends upon $V_a(r)$ for large r where $V_a(r)$ may not be known precisely. We assumed, however, that our method of

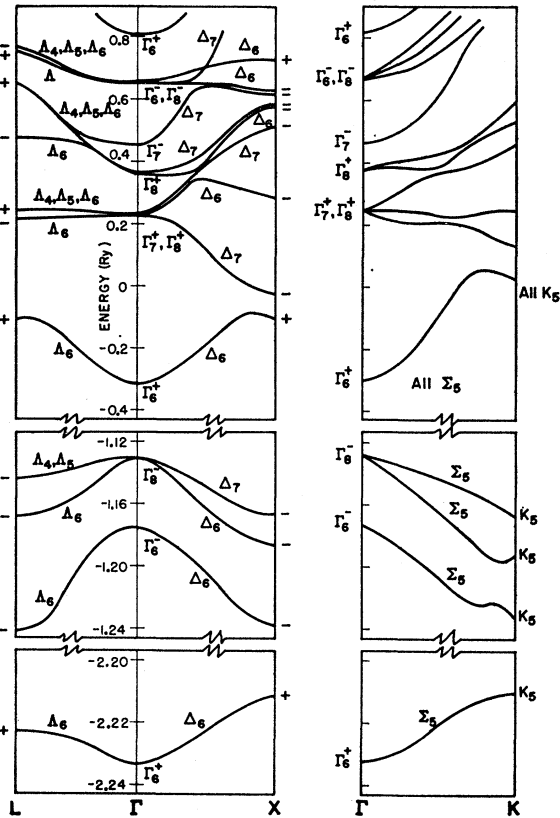


FIG. 3. Krypton band structure (with spin-orbit coupling). Spin-orbit splittings indicated for the conduction bands are schematic. Note the several changes in scale between 4s and 4p valence bands and conduction bands. Notation is that of Elliott (Ref. 31). Irreducible representations at L (and X) are given by $L_b^\pm(X_b^\pm)$, where b denotes the irreducible representation of $\Delta(\Delta)$ and only the sign (+ or -) is indicated. For example, the lowest X point shown is X_6^+ .

³³ T. O. Woodruff, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4; Phys. Rev. **103**, 1159 (1956).

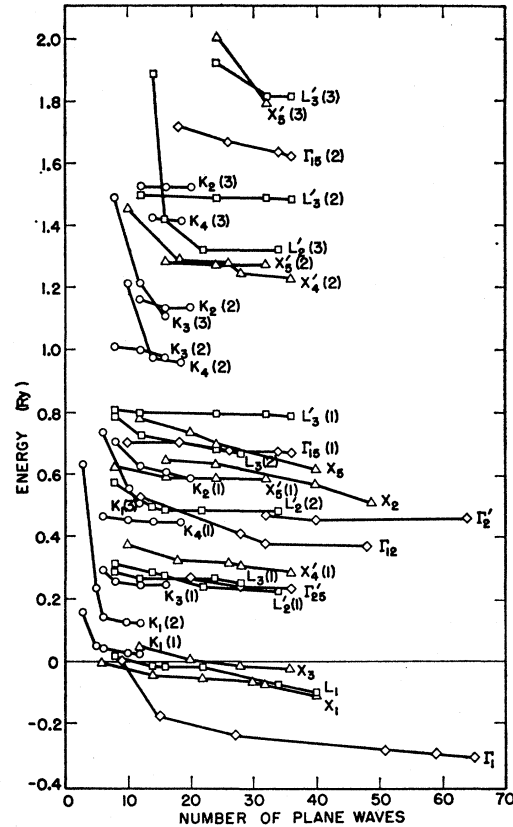


FIG. 4. Convergence of various OPW energies for krypton (see text).

constructing the crystal potential was a reasonably accurate one, and having chosen $V_a(r)$, we simply performed the integration. The resulting value for our potential was $v(0) = -1.274$ Ry.

Evaluation of the orthogonality matrix element $\langle \phi_i^\alpha, S_p^\alpha \rangle$ may be accomplished by expanding S_p^α in spherical harmonics. This is a standard approach and will not be discussed further here.

Results of the numerical calculation for the corrected Slater exchange potential are shown in Figs. 2 and 3, where the existence of spin-orbit splitting in the conduction bands has been indicated schematically. The shapes of the conduction bands are not a direct result of this calculation; those near symmetry points for the lowest conduction band are, however, a result of effective mass calculations, Sec. VI.

The convergence of various conduction band energies as a function of the number of plane waves involved in the matrix is shown in Fig. 4. Convergence is seen to be rather good for some states, not so good for others. For most points the use of from 5 to 7 sets of plane waves is sufficient for reasonable accuracy. Low-lying conduction band points are almost certainly computationally accurate (relative to each other) to within 0.05 Ry. The lowest point is probably accurate to

within 0.05 Ry. This estimate does not derive directly from observed convergence, which is not optimum because of slightly inaccurate core functions, but represents a reasonable extrapolation of the results shown in Fig. 4.

In the final results the highest valence and lowest conduction bands have a direct gap between Γ_1 and Γ_{15} (neglecting spin-orbit coupling) of 11.3 eV. The state Γ_1 was also computed using Slater and RBKS screened-Slater potentials. The results, in Ry, are for Slater, $E(\Gamma_1) = -0.73$; for RBKS, $E(\Gamma_1) = +0.15$. Corresponding predicted energy gaps between Γ_1 and Γ_{15} are 9.5 and 1.8 eV. The latter is clearly unreasonable; this is due to the breakdown of the core shift approach used in obtaining E_c 's, and demonstrates that the Hartree-Fock functions are not even approximate eigenfunctions of the RBKS Hamiltonian. Eigenfunctions of the RBKS Hamiltonian might more nearly resemble Hartree than Hartree-Fock functions. Thus, by comparing Hartree and Hartree-Fock eigenfunctions and energies, one may estimate core energies and eigenfunctions. Although the core shift approach is not valid, a calculation might still be made by the methods outlined in this paper.²² Tight-binding two-center integrals are not expected to depend too strongly on whether Hartree or Hartree-Fock (or RBKS) functions are used, and one should be able to estimate core energies. Convergence of the OPW conduction band states under these conditions might not be good, but one could at least estimate the shape and position of the conduction band.

As we have just implied, a pertinent point (previously discussed by Herring¹⁵ and by Woodruff³³) involves the importance of using in Eq. (16) core and valence wave functions which are accurate eigenfunctions of the crystal Hamiltonian. This is important in a theoretical sense for consistency, and in a practical sense to ensure reasonable convergence of OPW energies. We have studied this by computing certain valence and conduction states at Γ , X , and L by the OPW method. This yielded the following results: (a) At Γ_1 , seven sets of plane waves gave a valence energy only 0.2 Ry higher than that calculated by tight binding; more significantly, convergence of the Γ_1 conduction band state was much improved under this procedure. Similar results obtained at L_1 and X_1 . (b) At Γ_{15} , convergence with 7 sets of plane waves was to an energy 0.29 Ry higher than that calculated by tight binding. Indications were that at least one or more further sets might contribute nontrivially to E , and that the final position as determined by OPW would be closer to that determined by tight binding than is indicated here.

The position of the Γ_{15} conduction band state was in very close agreement (less than 0.1% different) with that calculated through orthogonalization to the valence band. This occurred because the amount of Γ_{15} valence band state included in Γ_{15} (conduction) was very small; that is, $\sum_p d_{c1,p} \Gamma_{15} \langle \phi_{val}^{\Gamma_{15}}, S_p^{\Gamma_{15}} \rangle$ was very

small, and behavior of the valence state did not affect that of the first conduction state very strongly. The states of the lowest conduction band shown in Figs. 2 and 3 were computed by the method discussed in these two paragraphs.

The same procedure for the Slater potential yielded a Γ_1 valence energy of -2.38 Ry, as compared with the tight-binding result -2.47 . For the RBKS potential $E(\Gamma_1)$ equals -1.19 Ry, as compared with the tight-binding result -0.85 . This is a further demonstration that the core shift procedure will not work accurately for large perturbations (such as the RBKS exchange), and that in fact there will be an important change in the wave function.

For further comparison of OPW and tight-binding results, we expanded the Γ_1 tight-binding function in OPW's and compared coefficients with the calculated Γ_1 OPW coefficients.²⁰ Agreement was reasonably good, which was not surprising since the corresponding energies were in close agreement.

The apparent discrepancy (of the order of tenths of a Ry) between the position of the Γ_{15} valence state calculated by tight-binding and OPW methods, and the uncertainty in the convergence of the first Γ_1 conduction state, lead us to estimate a computational uncertainty in the band gap of perhaps ± 1.0 eV. This of course does not represent the *physical* accuracy, since any result will depend strongly upon the crystal potential chosen.

The use of OPW perturbation theory was considered, but questions about its convergence and the desire for accurate determination of wave functions for effective mass calculations led us to abandon it. One would expect that in the case of solid argon⁷ the full OPW method would likewise be superior to the perturbation approach.

VI. THE EFFECTIVE MASS

As is well known, near points \mathbf{K}_m in \mathbf{k} space for which parity is a good quantum number (e.g., Γ , L , X) the one-electron energy is approximately given by

$$E_{\mathbf{k}}^n = E_{\mathbf{K}_m}^n + \frac{\hbar^2 k'^2}{2m} + \frac{\hbar^4}{m^2} \sum'_p \frac{|\langle \psi^{\nu, \mathbf{K}_m} | \mathbf{k}' \cdot \nabla | \psi^{n, \mathbf{K}_m} \rangle|^2}{E_{\mathbf{K}_m}^n - E_{\mathbf{K}_m}^p}, \quad (23)$$

where

$$\mathbf{k}' = \mathbf{k} - \mathbf{K}_m. \quad (24)$$

Thus an important result is demonstrated: Near such symmetry points, the E versus \mathbf{k}' relation is quadratic in \mathbf{k}' . The coefficient of k'^2 involved, however, is not, in general, $\hbar^2/2m$, but is an explicit function of the particular system and state considered. It is then relatively simple to speak of the E versus \mathbf{k} relation

in terms of the reciprocal effective mass tensor^{13,34}

$$\left(\frac{1}{m^*}\right)_{ij} = \pm \frac{1}{\hbar^2} \frac{\partial^2 E_k^n}{\partial k_i \partial k_j}, \quad (25)$$

where the + sign is associated with the effective mass of an electron, the - sign with that of a hole.

Calculation of valence band effective masses in the tight-binding formalism is very simple. Since one knows the explicit E versus \mathbf{k} dependence, one merely takes derivatives of the secular equation according to Eq. (25), and solves for (m^*/m) . Results of these calculations are listed in Table I (with spin-orbit interaction).

Application of effective mass theory to OPW conduction bands is, in general, more laborious than the simple procedure utilized for tight-binding valence bands.

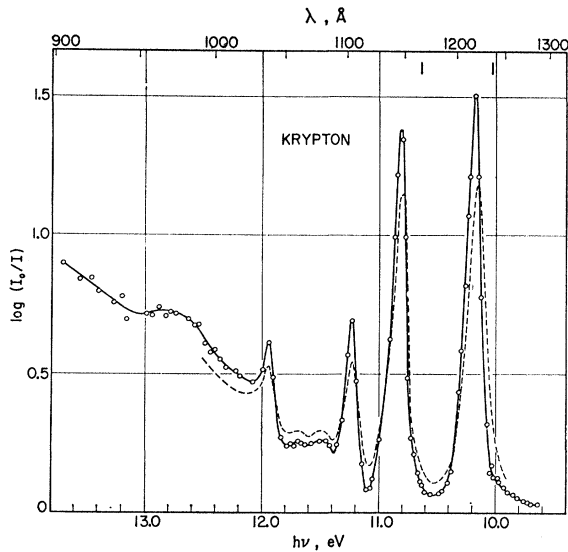


FIG. 5. Absorption spectrum of solid krypton (after Baldini, Ref. 11).

One does not have simple expressions for E versus \mathbf{k} , but knows E only at symmetry points. It is therefore necessary to use Eq. (23) and evaluate $\mathbf{k}' \cdot \nabla$ matrix elements involving the state of interest and other states. These other states include both valence and conduction states, and thus it is important to have fairly accurate wave functions. Fortunately, contributions from high-energy conduction band states are generally small.

Conduction band effective masses were computed in the lowest band for the points Γ_1 , L_1 , X_1 . We did not compute band shapes at K_1 . K is not a symmetry point, in the sense used here; that is, parity is not a good quantum number and E will not be a quadratic function of \mathbf{k}' . The shapes of the lower K_1 bands were schematically drawn in Figs. 2 and 3, based in part on analogy with the calculated results of Ref. 8.

³⁴ E. N. Adams, II, Phys. Rev. **92**, 18 (1953); W. Kohn and J. M. Luttinger, *ibid.* **98**, 915 (1955).

TABLE I. Effective hole masses for krypton valence bands (with spin-orbit coupling).

Point and direction	$(m^*/m)_{ii}$
$\Gamma_8^- \rightarrow \Delta_7$	+3.4
$\Gamma_8^- \rightarrow \Delta_6$	+1.5
$\Gamma_8^- \rightarrow \Delta_4, \Delta_5$	+7.1
$\Gamma_8^- \rightarrow \Delta_6$	+1.2
$X_7^- \rightarrow \Delta_7$	-3.9
$X_6^- \rightarrow \Delta_6$ (upper)	-3.5
$L_4^-, L_6^- \rightarrow \Delta_4, \Delta_5$	-7.5
$L_6^- \rightarrow \Delta_6$ (upper)	-4.9
$\Gamma_6^- \rightarrow \Delta_6$	+2.3
$\Gamma_6^- \rightarrow \Delta_6$	+2.3
$X_6^- \rightarrow \Delta_6$ (lower)	-2.3
$L_6^- \rightarrow \Delta_6$ (lower)	-1.6

In Table II are listed effective electron masses for various points in the lowest krypton conduction band. These numbers are probably accurate to within 0.1 electron mass. The masses at $\Gamma_1(\Gamma_6^+)$ are isotropic, those at $L_1(L_4^+)$ and $X_1(X_6^+)$ are anisotropic with two components each.

VII. COMPARISON WITH EXPERIMENT

Baldini's optical absorption results¹¹ for krypton are shown in Fig. 5; the dashed line represents measurements taken at 40°K, the solid line measurements at 20°K. He shows that the positions and strengths of the peaks between 10 and 12 eV are reasonably consistent with the properties of two series of simple Wannier excitons arising from the lowest conduction band and the spin-orbit split valence bands. On the basis of this model he deduces band gaps, reduced exciton masses, and exciton binding energies.

These quantities follow from consideration of the simple Wannier equation^{12,13}

$$h\nu_n = E_G - G/n^2, \quad n = 1, 2, 3, \dots, \quad (26)$$

where G , the exciton binding energy, equals $\mu\epsilon^{-2}$ Ry, ϵ is the dielectric constant, and μ is the reduced exciton mass in units of the electron mass,

$$1/\mu = m/m_e^* + m/m_h^*, \quad (27)$$

where m_e^* refers to the conduction band electron and m_h^* to the valence band hole.

We may use Eqs. (26) and (27), along with our theoretical results and an experimental value of ϵ , to predict optical absorption properties of krypton. We will expect some sort of transitions to take place invol-

TABLE II. Effective electron masses for krypton conduction bands.

Point and direction	$(m^*/m)_{ii}$
$\Gamma_1(\Gamma_6^+)$ (isotropic)	+0.6
$L_1(L_6^+)$ (1,1,1)	-2.3
$L_1(L_6^+)$ (1, 0, -1) or (1, -2, 1)	+0.6
$X_1(X_6^+)$ (1,0,0)	+2.0
$X_1(X_6^+)$ (0,1,0) or (0,0,1)	+0.8

TABLE III. Comparison with experiment. With the exception of the use of the experimental values of the krypton lattice constant and dielectric constant, the "theoretical" results are based entirely on *computed* band parameters. As noted in the text, the ratio of $G(\text{theor})$ to $G(\text{exp})$ is independent of ϵ since both involve the same value of ϵ , and therefore within the context of the Wannier model. We are comparing reduced masses only.

Series	Line	Theoretical		Experimental ^a	
		Energy (eV)	G (eV)	Energy (eV)	G (eV)
1	1	9.09		10.15	
	2	10.62	2.05	11.24	1.73
	3	10.91		11.48	
2	1	9.90		10.88	
	2	11.29	1.84	11.95	1.52
	3	11.55		...	

^a Reference 11.

ing the states at Γ , but we should also investigate the possibility of bound excitons being formed at the points L and X . At present the latter investigation cannot be carried out because a theory of Wannier excitons involving anisotropic or degenerate energy surfaces is complex and has not yet been developed to a point at which quantitative predictions pertinent to our problem can be made.^{33,35}

At the point Γ , we assume that Wannier excitons are constructed from the Γ_6^- and Γ_8^- valence states corresponding to the Δ_6 direction, and the Γ_6^+ conduction band state. Using our theoretical band gaps and effective masses, we may calculate binding energies and absorption energies for Wannier excitons. In our calculation we use for the dielectric constant $\epsilon=1.80$, which is a reliable value.¹¹ However, for small radius excitons ($n=1$) the effective dielectric constant might be somewhat less. At any rate, by using the same ϵ as does Baldini the ratio $G(\text{theor})/G(\text{exp})$ will be independent of ϵ and equal to $\mu(\text{theor})/\mu(\text{exp})$.

Pertinent quantities are listed in Table III, together with those of Baldini.¹¹ Disagreement is mainly of two sources: our theoretical energy gap is about 0.45 eV less than that inferred by Baldini, and we predict reduced masses for the first and second series to be 0.49 and 0.44, compared to Baldini's 0.41 and 0.36. Baldini's latter value may be too small; he uses the $n=1$ line to determine it, and the Wannier model is probably not accurate for such small-radius excitons. One thus does not expect to obtain quantitative agreement for $n=1$ lines. For the $n=2$ exciton, however, of the order of 40 lattice sites are enclosed in a sphere delineated by electron and hole, and the Wannier model might be expected to be reasonably valid. This point is discussed elsewhere.³⁶

³⁵ It seems likely that the techniques developed by Kohn and Luttinger (Ref. 34) for donor states in semiconductors can be applied to the Wannier exciton problem. To the author's knowledge, this has been done only for the case of nearly isotropic reduced masses, by J. J. Hopfield and D. G. Thomas, Phys. Rev. **122**, 35 (1961) and by R. G. Wheeler and J. O. Dimmock, *ibid.* **125**, 1805 (1962).

³⁶ G. Baldini and R. S. Knox, Phys. Rev. Letters **11**, 127 (1963).

Observed relative absorption strengths are in qualitative agreement with theory. Theoretically the oscillator strengths of the different lines should go as n^{-3} on the Wannier model¹³; according to Baldini,¹¹ the observed ratio for $n=1$ and $n=2$ lines is about 4 (whereas it should be 8). This is not considered a serious discrepancy, however, since as mentioned the $n=1$ lines are not expected to be in quantitative accord with the Wannier model. Linewidths are also consistent with a Wannier picture.⁹ Agreement is generally rather good, and it appears that the interpretation of the krypton lines as corresponding to $n=1, 2, 3, \dots$ Wannier excitons at Γ is reasonable. Further support for this sort of interpretation arises from a study³⁶ by Baldini and Knox of the optical properties of mixed rare gas crystals.

Further theoretical work might include a study of xenon. One might infer that the band structure of xenon would resemble that of krypton, based upon similarities between argon^{7,8} and krypton. It would then probably be worthwhile to attempt to determine where the differences and similarities between krypton and xenon would lie, and explain the xenon absorption structure on the basis of these. For example, the large spin-orbit interaction in xenon might cause the $5p$ valence band to be split into two nonoverlapping parts. Also, the formation of excitons at the points L or X might be of importance.

Several experiments may be suggested. Photoconductivity studies would be useful in helping to identify band-to-band transitions and other phenomena associated with conductivity. The study of optical properties of rare gases doped with impurities such as hydrogen and sodium could yield among other things information regarding the position of impurity levels within the forbidden gap. The relationship between the optical properties of annealed and nonannealed samples of solid rare gas might be studied further, to understand better how defects in crystal structure and excitons are related.

VIII. SUMMARY AND CONCLUSIONS

It has been shown that the combined tight binding and full OPW methods yield a convergent set of energy bands for the rare gas solids. The calculation which we have performed contains several important features which have not generally been included in earlier work. The exchange potential has been constructed in a new manner as a sum of quasiautomic potentials whose sum resembles the known crystal free-electron effective exchange potential. The shifts of core and valence quasiautomic energies in this potential have been taken into account by perturbation theory. The spin-orbit interaction has been incorporated into the tight-binding formalism and parameters have been explicitly calculated. The full OPW method has been utilized to calculate rare gas conduction bands, and has been shown to be capable of handling valence bands which were

thought to be amenable only to tight-binding or atomic-like treatments, in contrast with previously held notions.^{7,8} The success of the Wannier exciton model in interpreting Baldini's krypton results¹¹ suggests that other electronic properties of the solid rare gases are capable of being understood in the framework of effective-mass theory.

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Plasma Resonance Absorption in Thin Metal Films*

A. J. McALISTER

AND

E. A. STERN

University of Maryland, College Park, Maryland

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The transmission of p - and s -polarized light through thin silver films as a function of wavelength and angle of incidence has been measured. As predicted, a dip in transmission occurs in the vicinity of the plasma frequency only for the p -polarized light. This dip is associated with the excitation of a collective-type surface plasma mode in the thin film by the electromagnetic wave. The plasma frequency of the film can be accurately determined from this dip to occur at 3.80 eV.

I. INTRODUCTION

WHEN a charged particle passes from one dielectric medium to another, electromagnetic radiation is emitted because of the rearrangement of the induced surface charges. This "transition radiation" was first calculated by Ginzburg and Frank¹ and then extended by other authors.^{2,3} Ferrell⁴ has shown that, for the case of a thin metal film, a simple physical picture can be used to predict a peak in the transition radiation around the plasma frequency. Subsequently, other authors⁵⁻⁸ have shown that this peak is also predicted by the usual theory of the transition radiation from a metal slab in

the limit of small thickness. More recently, a quantum-mechanical calculation of this peak has also been made.⁹ This predicted peak in the transition radiation has been seen experimentally.¹⁰

On the basis of Ferrell's physical picture for the peak, it was predicted that electromagnetic radiation of the correct polarization and non-normal incidence would show anomalous behavior around the plasma frequency in interacting with thin metal films.¹¹ In the next section we describe in more detail the physical ideas involved and present the theoretical expressions which describe the interaction of electromagnetic waves with thin metal films. The last section describes the experimental results which show the expected behavior and gives a discussion of the results.

II. PHYSICAL CONSIDERATIONS

Consider a metal film of an ideal electron gas of thickness d . If the film is thin enough, then the type of oscillation in the film illustrated in Fig. 1 should occur. This

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