results we need in our calculations are the following:

$$q_{15}=q_{51}=-q'_{35}=-\sqrt{2}(D+D'), \tag{B20}$$

$$q'_{15}=-q_{35}=q_{53}=2\sqrt{2}\,D', \tag{B21}$$

$$q_{34}=2\sqrt{\tfrac{2}{5}}\,D, \tag{B22}$$

$$q'_{34}=-\sqrt{\tfrac{2}{5}}(D+5D'), \tag{B23}$$

$$q_{54}=(2/\sqrt{5})(D+3D'), \tag{B24}$$

$$q'_{54}=(2/\sqrt{5})(D'+2D), \tag{B25}$$

$$q_{55}=0, \tag{B26}$$

$$q'_{55}=-2\sqrt{3}\,D'. \tag{B27}$$

In these equations the unprimed constants refer to a transition from a ground-state sublevel to a level designated by a $\Psi$ in Table X while the primed quantities have a final state described by a $\Phi$.

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†NATO Fellow. On leave of absence from Institut de Physique, Université de Liège, Liège, Belgium.

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# The Excitonic Molecule

W. F. Brinkman, T. M. Rice, and Brian Bell*

*Bell Laboratories, Murray Hill and Holmdel, New Jersey*

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The binding energy of the excitonic molecule is calculated as a function of electron-to-hole mass ratio and of anisotropy in the hole bands. A variational wave function is used which is a product of a Hylleraas and Ore correlated exciton function and an overlap function of the hole-hole separation. The results are tabulated for CuCl, CuBr, $Cu_2O$, and for a number of II-VI compounds.

## I. INTRODUCTION

The possibility of binding four light particles into a neutral molecule was first demonstrated by Hylleraas and Ore.[1] They considered the complex of two electrons and two positrons and obtained a small binding energy relative to two positronium atoms. Subsequently, Lampert[2] raised the possibility that the analog of the positronium molecule would exist in a semiconductor involving two Wannier excitons. Since that time, there have been a number of claims to have observed emission lines from the decay of excitonic molecules (or biexcitons). The evidence appears strongest in the direct-gap semiconductors CuCl[3-5] and CuBr.[3,6] The observation of molecules in $Cu_2O$

by Gross and Kreingold[7(a)] has recently been challenged.[7(b)] In Si and Ge, however, it is now generally believed that the line, originally identified by Haynes[8] as due to a decay of an excitonic molecule, is from droplets of a metallic electron-hole liquid.[9] In this paper we will be concerned with variational calculations of the binding energy of an excitonic molecule and will comment only briefly on the experimental situation. Such calculations are useful in aiding the identification of an emission line from an excitonic molecule. It is also of interest to compare the energies of the molecule with that of the metallic electron-hole liquids[10–12] and to determine which state is more likely at high densities of electrons and holes.

Since the electron ($m_e$) and hole ($m_h$) masses in semiconductors are not identical, it is necessary to consider the binding energy as a function of the mass ratio $\sigma = m_e/m_h$. In addition, in many cases of interest the masses are quite anisotropic. The first attempt to treat the former problem was that of Sharma.[13] He considered the binding energy of the excitonic molecule as a function of $\sigma$ for values between 0 (the hydrogenic limit) and 1 (the positronium limit). He found a number of unusual results. In the first place, in his calculations there was no binding between $0.2 < \sigma < 0.4$ and secondly, his value for the positron limit was a factor of 8.5 larger than the value found by Hylleraas and Ore.[1] The former results were criticized by Wehner,[14] who showed that the slope of the binding energy as $\sigma \to 1$, was in error. Recently, Adamowski *et al.*[15] have proven that if the molecule is bound at $\sigma = 1$, it is bound for all values of $\sigma$ in the interval $0 \le \sigma \le 1$. Sharma's[13] result for the positronium molecule is also very different to the binding energy which we and other workers[16] obtain and is, we believe, in error.[16]

Recently, Akimoto and Hanamura[16] have investigated the range $0 < \sigma < 1$ for isotropic electron and hole masses. They used a variational wave function which was a product of the Hylleraas-Ore wave function and an overlap function for the holes. In the limit $\sigma \to 0$, the choice of a $\delta$ function for the overlap function leads to a wave function for the hydrogen molecule previously considered by Inui[17] and Nordsieck[18] and gives a binding energy per electron of 0.299 Ry, as compared to the exact value of 0.348 Ry. The binding energy decreased monotonically with increasing $\sigma$ to a value, at $\sigma = 1$, of 0.018 of the positronium rydberg which is very close to the value obtained by Hylleraas and Ore.[1,19] In this paper we will always work in energy units of the rydberg of the single atom, e.g., the positronium rydberg equals 6.8 eV.

In this paper we investigate the effect both of unequal masses and anisotropy of the heavier mass on the ground state of the excitonic molecule. In Sec. II we consider first isotropic masses. We use a variational wave function which is similar to that employed in Ref. 16 but with a more general overlap function. We derive a wave equation for the overlap function and find a binding energy which is significantly larger than that of Ref. 16 in the interval $0.2 < \sigma < 1$. In the limit $\sigma \to 1$ our method yields a binding energy of 0.029 of the positronium rydberg, which is a considerable improvement over previous estimates.[1,16] Recently Akimoto and Hanamura[20] have obtained a value of 0.027, very close to the value reported here.

In Sec. III we extend our calculation to anisotropic band structures. In group-II-VI compounds, such as CdS and CdSe, a considerable simplification can be made by noting that the electron masses, which are much lighter than the hole masses, are almost isotropic. Since the light electron mass dominates in the reduced mass entering a single exciton, the exciton wave function will be very close to isotropic. Therefore, it is reasonable to include the anisotropy only in the overlap function of the holes. This simplifies the problem considerably, since a wave equation can be derived for the overlap function which will involve the same potential as for isotropic bands. We have carried out detailed calculations for an isotropic electron band and an ellipsoidal hole band with masses $m_\perp$ and $m_\parallel$ for the range of parameters $0 < \sigma < 1$ and $0 < \gamma \, (= m_\perp / m_\parallel) < 1$. We have confined our attention to ellipsoidal band structures for the holes. The complicated valence-band structure of the group-III-V compounds presents a formidable obstacle to a detailed calculation and we have not included the anisotropy in these compounds.

In Sec. IV we review the experimental situation and quote values of the binding energy in CuCl, CuBr, and $Cu_2O$, and also in the group-II-VI compounds CdS, CdSe, and ZnS. Excitonic molecules are observed by examining the emission spectrum. The most likely processes which will show up as sharp lines in emission are those in which an excitonic molecule decays into a photon and an exciton in a 1*s* singlet or a 2*s*, 2*p* state. The decay process into a photon and free electron and hole will be difficult to identify since the spread of kinetic energies of the electron and hole will lead to a linewidth of the order of an exciton rydberg.

## II. ISOTROPIC BANDS

In the effective mass approximation, the Hamiltonian for a system of two electrons of mass $m_e$ and two holes of mass $m_h$ is

$$H = -\frac{\mu}{m_e}(\nabla_1^2 + \nabla_2^2) - \frac{\mu}{m_h}(\nabla_a^2 + \nabla_b^2) + V\,, \tag{2.1}$$

where the potential energy $V$ is given by

$$V=\frac{2}{r_{12}}+\frac{2}{r_{ab}}-\frac{2}{r_{1a}}-\frac{2}{r_{1b}}-\frac{2}{r_{2a}}-\frac{2}{r_{2b}}\ . \tag{2.2}$$

We have denoted the electron (hole) coordinates by the subscripts 1 and 2 ($a$ and $b$), and $|\vec{r}_1-\vec{r}_2|\equiv r_{12}$, etc. In (2.1), and throughout this paper, the unit of length is the exciton Bohr radius $a_x=\epsilon_0\hbar^2/\mu e^2$, and the unit of energy is the exciton rydberg $R_x=\mu e^4/2\epsilon_0^2\hbar^2$, with $\epsilon_0$ being the static dielectric constant of the crystal and $\mu$ being the reduced mass ($\mu^{-1}=m_e^{-1}+m_h^{-1}$).

It is not possible to solve the four-body problem exactly and we therefore employ a variational technique. Since in the range of parameters we are studying the hole mass is heavier than the electron mass, the true wave function will be more sensitive to the distance between the holes than to the distance between electrons. Therefore we choose a trial function of the form

$$\Psi=[\psi(r)/S(R)]F(R)\ , \tag{2.3}$$

with

$$S^2(R)\equiv\int\psi^2(r)d\tau_r\ . \tag{2.4}$$

Here $R$ refers to the hole-hole separation and $\psi$ is a function of the electron-hole distances only. These distances are denoted by the single index $r$.

The energy of the ground state $E_{\text{mol}}$ is found by minimizing the ratio

$$E=\int d^3R\,d\tau_r\,F(R)\,\frac{\psi(r)}{S(R)}\,H\,\frac{\psi(r)}{S(R)}\,F(R)\Big/\int d^3RF^2(R)\ . \tag{2.5}$$

Taking the functional derivative with respect to $F$ gives a wave equation of the form

$$-(2\mu/m_h)\nabla^2_{\mathrm{R}}F(R)+U_\sigma(R)F(R)=EF(R)\ , \tag{2.6}$$

where the effective hole-hole potential function $U_\sigma(R)$ is given by

$$U_\sigma(R)=\int(\psi/S)H(\psi/S)\,d\tau_r\ . \tag{2.7}$$

By choosing the function $\psi/S$ to be normalized for all values of $R$, we have eliminated all terms involving products of the gradient operator.

### A. Hole-Hole Interaction

The function $U_\sigma(R)$ is the effective hole-hole potential energy. To evaluate it we follow Hylleraas and Ore[1] and choose for $\psi$ the function

$$\psi=2e^{-(s_1+s_2)/2}\cosh\tfrac{1}{2}\beta(t_1-t_2)\ , \tag{2.8}$$

with the definitions

$$s_1=k(r_{1a}+r_{1b}),\quad s_2=k(r_{2a}+r_{2b})\ ,$$

$$t_1=k(r_{1a}-r_{1b}),\quad t_2=k(r_{2a}-r_{2b})\ .$$

The parameters $\beta$ and $k$ are to be determined variationally. In this function $\beta$ controls the degree to which a given electron is shared between the two holes. The value $\beta=1$ corresponds to two separate excitons with each electron associated with one hole, while at $\beta=0$ each electron is equally shared by the two holes:

$$U_\sigma(R)=-\frac{\mu}{m_e}\int\frac{\psi}{S^2}(\nabla_1^2+\nabla_2^2)\psi\,d\tau_r-\frac{\mu}{m_h}\int\frac{\psi}{S}(\nabla_a^2+\nabla_b^2)\frac{\psi}{S}\,d\tau_r+\int V\frac{\psi^2}{S^2}\,d\tau_r\ . \tag{2.9}$$

Now

$$\nabla_a^2\frac{\psi}{S}=\frac{1}{S}\nabla_a^2\psi-\frac{2}{S}(\vec{\nabla}_a\psi)\cdot(\vec{\nabla}_aS)+\frac{2}{S^3}\psi(\vec{\nabla}_aS)^2-\frac{\psi}{S^2}\nabla_a^2S\ , \tag{2.10}$$

but from (2.4) we know that

$$\int\psi\vec{\nabla}_a\psi\,d\tau_r=S\vec{\nabla}_aS\ .$$

Upon integration the two middle terms of (2.10) cancel and we obtain the result

$$\int\frac{\psi}{S}\nabla_a^2\frac{\psi}{S}\,d\tau_r=\int\frac{\psi}{S^2}\nabla_a^2\psi\,d\tau_r-S^{-1}\nabla_a^2S\ . \tag{2.11}$$

In their original calculation Hylleraas and Ore[1] used the form of Eq. (2.8) as their trial function, i.e., treating both electrons and holes identically. This means that, for the positronium limit, the kinetic energy contributions from the electrons and holes are equal.[19] In our case we distinguish between electrons and holes and the form of the kinetic energy terms changes. In Appendix A we show that, for the form of $\psi$ used,

$$(\nabla_a^2+\nabla_b^2)\psi=(\nabla_1^2+\nabla_2^2)\psi-\tfrac{1}{2}k^2(\hat{r}_{1a}-\hat{r}_{1b})\cdot(\hat{r}_{1b}-\hat{r}_{1a})(1-\beta^2)\psi\equiv(\nabla_1^2+\nabla_2^2)\psi+T_1(r)\ , \tag{2.12}$$

where $\hat{r}_{1a}$ is a unit vector.

Finally we have

$$U_\sigma(R)=-\int\frac{\psi}{S^2}(\nabla_1^2+\nabla_2^2)\psi\,d\tau_r-\frac{\mu}{m_h}\int\frac{\psi\,T_1(r)\,d\tau_r}{S^2}+\frac{\mu}{m_h}\frac{(\nabla_a^2+\nabla_b^2)S}{S}+\int\frac{V\psi^2}{S^2}\,d\tau_r\ . \tag{2.13}$$

The evaluation of the first and last terms in (2.13) has been carried out by Nordsieck[13] and Inui.[12] All contributions are straightforward except for the Coulomb repulsion between the electrons. This has been evaluated by Nordsieck using an expansion in spherical harmonics. This expansion is valid for small and intermediate hole separations but breaks down at large $R$. In the large-$R$ limit it is possible to evaluate the integrals explicitly as a power series in $R^{-1}$. This is carried out in Appendix B. We have interpolated between these two regions by adding a roundoff term to the Nordsieck expansion.[21] This procedure was checked by requiring that the choice $F(R) = S(R)$ reproduce the Hylleraas-Ore result. We wish to point out that in our variational calculations $F(R)$ is shorter range than $S(R)$ and the results are not sensitive to the detailed form of the interpolation. The third term in (2.13) can be evaluated in a straightforward manner. In Appendix A we give the evaluation of the second term which is the difference between the electron and hole kinetic energies.

This completes the evaluation of $U_\sigma(R)$. The result for the case $\beta^2 = 0.5$ and $k = 1.18$ is shown in Fig. 1. For comparison we show also the corresponding Heitler-London[22] potential which is given by the choice $\beta = k = 1$. There is a significant difference between the two forms and indeed we have found it impossible to obtain binding at $\sigma = 1$ with the Heitler-London form.

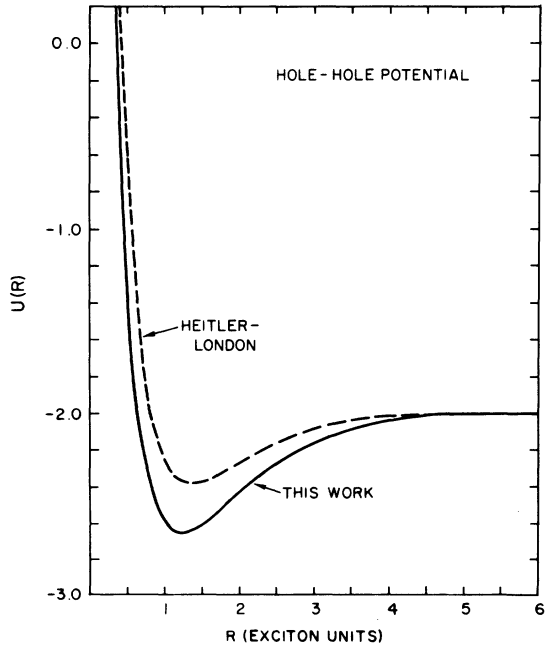

FIG. 1. Effective interaction between two excitons as a function of the separation of the two holes. The Heitler-London approximation corresponds to $k = \beta = 1$, while for the solid curve $k = 1.18$ and $\beta^2 = 0.5$.

TABLE I. Parameters used in the calculations with $\gamma = 1$ for various values of $\sigma$. The definitions of the various parameters are contained in Eqs. (2.8) and (2.14) and the discussion thereafter.

| $\sigma$ | $n$ | $k$ | $\beta$ | $A$ | $B$ | $C$ |
|---|---|---|---|---|---|---|
| 1.0 | 1 | 1.18 | 0.655 | 1.14 | 0.36 | 0.39 |
| 0.5 | 1 | 1.18 | 0.68 | 1.11 | 0.38 | 0.16 |
| 0.3 | 2 | 1.18 | 0.70 | 0.72 | 0.32 | 0.52 |
| 0.2 | 2 | 1.18 | 0.71 | 0.67 | 0.33 | 0.29 |
| 0.1 | 3 | 1.18 | 0.74 | 0.47 | 0.29 | 0.54 |
| 0.05 | 4 | 1.14 | 0.76 | 0.35 | 0.29 | 0.98 |

### B. Isotropic Valence Bands

To find the energy we must solve (2.5) by a suitable choice of the envelope function $F(R)$. If we put $F(R) = S(R)$ we will recover the results of Hylleraas and Ore in the equal-mass limit. This provides a check on the routines used to calculate the energy. In the present calculation we used the function

$$F(R) = R_1^n e^{-R_1} + C e^{-BR_1} , \tag{2.14}$$

where $R_1 \equiv R/A$ and $A$, $B$, and $C$ are variational parameters. The index $n$ was varied also but its variation was restricted to integer values. The first term is identical to that used by Akimoto and Hanamura.[16] In carrying out the variational calculation with respect to the six parameters in our wave function, viz., $k$, $\beta$, $A$, $B$, $C$, and $n$, we have found it relatively simple to obtain a minimum value with an accuracy of $0.001 R_x$ but difficult to go beyond this limit. All values we quote have an uncertainty of this magnitude associated with them. Since the wave function [Eq. (2.14)] is the sum of two terms the optimum value of the mixing coefficient $C$ was determined for each value of the other parameters by solving a $2\times 2$ determinant. In Table I we list for six values of $\sigma$ the optimum values of our parameters.

In the equal mass or positronium limit, we find the binding energy to be $0.029 R_x$, which is significantly larger than the values $0.017 R_x$ and $0.018 R_x$ obtained in Refs. 1 and 16, respectively. Recently Akimoto and Hanamura[20] have obtained a value of $0.027 R_x$, very close to that reported here. It is interesting to consider why (2.14) should produce more binding than the calculation of Hylleraas and Ore.[1] A comparison of the envelope functions is given in Fig. 2. It is seen that (2.14) is more localized about the potential minimum than the normalization function $S(R)$. The presence of the dip at $R = 0$ does not lower the energy significantly. In the hydrogen molecule the incorporation of the electron-electron correlation in the wave function gives an important contribution to the binding.[23]

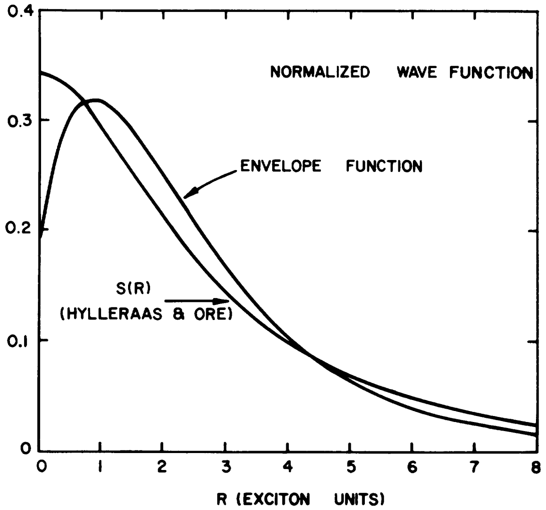

FIG. 2. Comparison of the wave function $F(R)$ used in the present calculation with the normalization integral $S(R)$ of the Hylleraas-Ore trial function. Their calculation is obtained from ours by setting $F(R)=S(R)$. The functions are normalized so that $\int_0^\infty F^2(R)R^2\,dR=1$.

However, in the three-body problem of two electrons and a positron, Hylleraas[24] found that including the electron-electron correlation gave only a very small improvement in the binding. The large extent of the wave functions in the positron limit undoubtedly is the reason for the insensitivity to short-range repulsion between the particles of like charge. Finally, we wish to comment that our wave function is not symmetric in electrons and holes and incorporation of this symmetry will lower the energy further in the equal-mass limit.

The energy of the excitonic molecule as a function of the mass ratio $\sigma=m_e/m_h$ is plotted in Fig. 3, where it is compared with the results of Akimoto and Hanamura.[16] The results can be summarized as follows: (i) The binding energy in the interval $0.2<\sigma<1$ is appreciably larger than that of Ref. 16. (ii) The slope at $\sigma=1$ is approximately zero, as it should be from symmetry considerations (see Ref. 14). (iii) As $\sigma\to 0$ the asymptotic form is

$$E(\sigma)=-2.30+0.94\sigma^{1/2}\,. \tag{2.15}$$

This is to be compared with the exact expression of the hydrogen molecule quoted in Ref. 14:

$$E(\sigma)=-2.34+0.76\sigma^{1/2}\,. \tag{2.16}$$

## III. ANISOTROPIC VALENCE BANDS

In this section we will consider the effects of the anisotropy of the valence bands upon the energy of the molecule. For the materials of interest the conduction band is essentially isotropic and the electron mass is light compared to that of the hole. Thus the reduced mass of the exciton is almost isotropic. In our variational form (2.3) we will take $\psi$ to be a function only of the isotropic variables $r$. This greatly simplifies the problem. The hole-hole potential is now also isotropic. We will consider only the case where the hole bands are ellipsoidal, the hole mass parallel to the $c$ axis, $m_\parallel$, being heavier than the mass in the perpendicular plane, $m_\perp$.

In the hole-hole potential $U_\sigma(R)$ the characteristic hole mass which enters is the optical-mass average

$$m_h^{-1}=\tfrac{1}{3}(2m_\perp^{-1}+m_\parallel^{-1}) \tag{3.1}$$

and the electron-hole mass ratio $\sigma(=m_e/m_h)$. Defining an anisotropy parameter $\gamma=m_\perp/m_\parallel$, we can write the wave equation (2.6) in terms of $\sigma$ and $\gamma$ as

$$-\frac{6\sigma}{(2+\gamma)(1+\sigma)}\nabla_\perp^2F(\vec{R})-\frac{6\sigma\gamma}{(2+\gamma)(1+\sigma)}\nabla_\parallel^2F(\vec{R})+U_\sigma(R)F(\vec{R})=EF(\vec{R})\,, \tag{3.2}$$

where the subscripts refer to the direction of $\vec{R}$ relative to the $c$ axis. Note $U_\sigma(R)$ is independent of $\gamma$. We have again used a variational technique to solve the anisotropic wave equation (3.2). The functional form $F(\vec{R})$ can be simply generalized to the anisotropic case by the replacement in (2.14)

$$R_1=(R_\perp^2/A_1^2+R_\parallel^2/A_2^2)^{1/2}\,, \tag{3.3}$$

where $A_1$ and $A_2$ are variational parameters which replace the single parameter $A$ in the isotropic

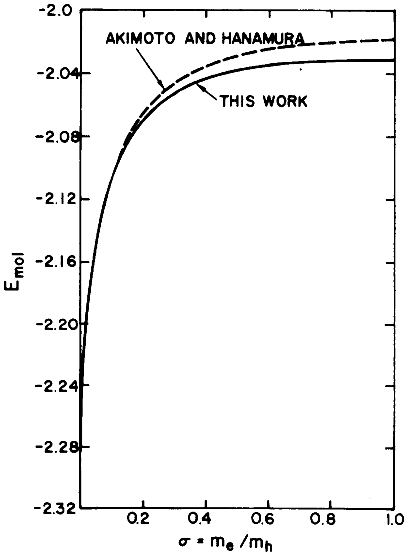

FIG. 3. Molecular binding energies as a function of $\sigma$. The energy is in units of the exciton binding energy. The dashed line is the result of Akimoto and Hanamura (Ref. 16).

TABLE II. Variational parameters used for the $\gamma = 0.1$ calculations as a function of $\sigma$. The parameters $n$, $k$, and $\beta$ are the same as those listed in Table I for the different values of $\sigma$. The parameters $A_1$ and $A_2$ are defined in Eq. (3.3).

| $\sigma$ | $A_1$ | $A_2$ | $B$ | $C$ |
|---|---|---|---|---|
| 1.0 | 1.38 | 0.70 | 0.47 | 0.26 |
| 0.5 | 1.28 | 0.71 | 0.46 | 0.09 |
| 0.3 | 0.80 | 0.49 | 0.35 | 0.39 |
| 0.2 | 0.75 | 0.46 | 0.36 | 0.21 |
| 0.1 | 0.51 | 0.34 | 0.30 | 0.39 |
| 0.05 | 0.37 | 0.28 | 0.27 | 0.62 |

case. Such a replacement has been employed in the past to treat anisotropic wave equations, viz., Kohn and Luttinger's treatment[25] of the anisotropic wave equation in a Coulomb field. The variation with respect to the seven parameters was carried out as follows. For each value of $\sigma$ the optimum values at $\gamma = 1$ were determined previously. As $\gamma$ varied away from 1 we held the parameters $k$, $\beta$, and $n$ fixed at their optimum values at $\gamma = 1$ and varied the four parameters $A_1$, $A_2$, $B$, and $C$. The following trends were noted: The parameter $A_1$ increased as $\gamma$ decreased while $A_2$ decreased. The parameter $B$ was approximately constant. In Table II we list the optimum values obtained at $\gamma = 0.1$ for each value of $\sigma$.

As $\gamma \rightarrow 0$ the forms (2.14) and (3.3) for the envelope function $F(\vec{R})$ become inaccurate. The two holes become a fixed distance apart along the $c$ direction while the function (2.14) gives them a distribution with a maximum value at the origin.

In the limit $\gamma \rightarrow 0$ we may employ an adiabatic approximation to solve Eq. (3.2), taking the form

$$F(\vec{R}) = f(R_\perp, R_\parallel)\chi(R_\parallel) . \tag{3.4}$$

The resulting equation for $f$ is

$$-\frac{6\sigma}{(2+\gamma)(1+\sigma)} \nabla_\perp^2 f(R_\perp, R_\parallel) + U_\sigma(R) f(R_\perp, R_\parallel) = \lambda_\sigma(R_\parallel) f(R_\perp, R_\parallel) . \tag{3.5}$$

This equation is now solved for a fixed value of $R_\parallel$ by a variational technique using the forms (2.14) and (3.3) for $f$. In this way an energy function $\lambda_\sigma(R_\parallel)$ is determined. This function has a minimum at a finite value of $R_\parallel = R_\parallel^0$. Near this value we may write

$$\lambda_\sigma(R_\parallel) = \lambda_{\sigma,0} + \lambda_{\sigma,1}(R_\parallel - R_\parallel^0)^2 . \tag{3.6}$$

The minimum value $\lambda_{\sigma,0}$ gives the molecular binding energy as $\gamma \rightarrow 0$, while the curvature determines the leading correction in $\gamma$. The effective equation in the $c$ direction is simply a one-dimensional harmonic oscillator. We obtain the result, in the limit $\gamma \rightarrow 0$:

$$E_{\text{mol}}(\sigma, \gamma) = \lambda_{\sigma,0} + [3\sigma/(1+\sigma)]^{1/2} \lambda_{\sigma,1}^{1/2} \gamma^{1/2} + O(\gamma) .$$

In order to obtain the binding energy we must subtract off the energy of two separate excitons. In the isotropic limit or $\gamma = 1$, this energy is simply 2, since our unit of energy is the binding energy of the isotropic exciton with mass ratio $\sigma$. However, if $\gamma \neq 1$, the exciton binding energy $E_x$ will vary as a function of $\gamma$. The values of $E_x(\sigma, \gamma)$ may be readily calculated from the results of Kohn and Luttinger[25] and Faulkner.[26] [Note that their notation differs from ours. Their parameter $\gamma = (3\sigma\gamma + 2 + \gamma)/(3\sigma + 2 + \gamma)$ and their energy unit is equal to $(2 + \gamma + 3\sigma)/(1+\sigma)(2+\gamma)$ in our units.]

In Fig. 4 we plot the binding energy $E_B$, defined as

$$E_B = E_{\text{mol}}(\sigma, \gamma) - 2E_x(\sigma, \gamma) ,$$

which we obtain in this way. These values are also listed in Table III. There are several comments to be made. First, for $\sigma = 1$, the curve shows no binding in the range $0.002 < \gamma < 0.3$. This is undoubtedly due to a failure of our approximation in this limit. In our calculations $|E_{\text{mol}}|$ increases as $\gamma$ decreases but this increase is more

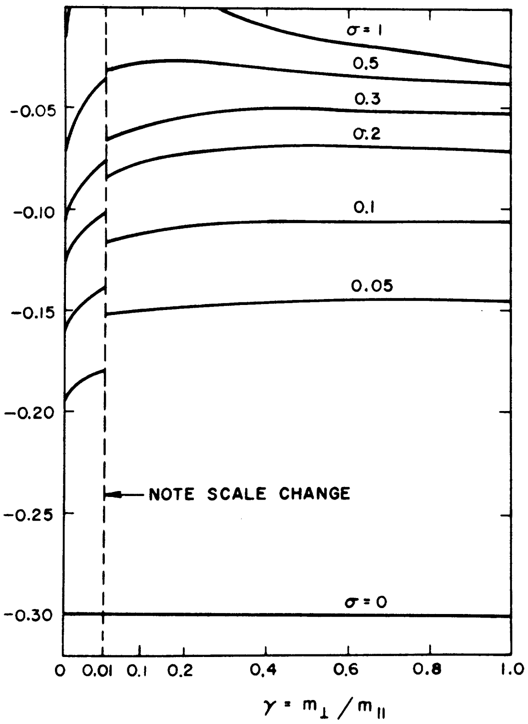

FIG. 4. Plot of the excitonic molecule binding energies as a function of $\sigma$ and $\gamma$. The approximation scheme used here clearly breaks down in the region of small $\gamma$ and $\sigma \sim 1$. Note that the binding energies are almost constant until $\gamma < 0.1$. Energies are in units of the isotropic ($\gamma = 1$) exciton binding energy.

TABLE III. Molecular binding energies for various values of $\sigma = m_e/m_h$ and $\gamma = m_\parallel/m_\perp$. Here $m_h^{-1} = \frac{1}{3}(2m_\perp^{-1} + m_\parallel^{-1})$ and the unit of energy is the exciton rydberg $= \mu e^4/2\epsilon_0^2\hbar^2$ where $\mu^{-1} = m_e^{-1} + m_h^{-1}$. The additional binding of the excitons due to the anisotropy of the hole mass has been subtracted from the calculated energies as discussed in the text.

| $\gamma$ | 0.05 | 0.1 | 0.2 | 0.3 | 0.5 | 1.0 |
|---|---|---|---|---|---|---|
| 0.0 | 0.195 | 0.160 | 0.130 | 0.110 | 0.078 | 0.015 |
| 0.01 | 0.152 | 0.115 | 0.083 | 0.066 | 0.031 | −0.028 |
| 0.1 | 0.148 | 0.112 | 0.076 | 0.058 | 0.027 | −0.029 |
| 0.2 | 0.148 | 0.109 | 0.072 | 0.054 | 0.026 | −0.007 |
| 0.4 | 0.146 | 0.106 | 0.068 | 0.050 | 0.030 | 0.010 |
| 0.6 | 0.145 | 0.105 | 0.068 | 0.049 | 0.033 | 0.018 |
| 0.8 | 0.145 | 0.106 | 0.069 | 0.052 | 0.034 | 0.023 |
| 1.0 | 0.145 | 0.106 | 0.070 | 0.052 | 0.038 | 0.029 |

than canceled by the increase in $E_x$. In the variational wave function the excitons in $\psi$ are taken as isotropic and the anisotropy only enters in via the overlap function $F(\vec{R})$. In this region, however, individual excitons are far from isotropic and our approximate wave function is not accurate. The region of experimental interest, however, is $\sigma \sim 0.1$ for which our approximations are substantially better. The excitons are very nearly isotropic for all values of $\gamma$ when $\sigma = 0.1$ and the correction to the exciton binding energy never exceeds 0.4%, whereas the molecular binding energy is ≈10%. The major result of our calculations is that $E_B$ is independent of $\gamma$ over most of the range of $\gamma$. While the limiting value $E_B(\sigma, 0)$ can be increased by as much as $0.05R_x$, this increase is very rapidly reduced by the zero-point motion in the $c$ direction. From Fig. 4 we conclude that we do not expect major shifts in the binding energy of excitonic molecules from anisotropic effects. This conclusion is contrary to some recent speculation by Shionoya *et al.*[27]

## IV. COMPARISON WITH EXPERIMENT

The calculations presented in Sec. II can be applied to the cubic materials CuBr,[3,6] CuCl,[3-5] and $Cu_2O$.[7(a),7(b)] The mass ratios, the exciton binding energies, and the predicted binding energy of the molecule are listed in Table IV. The experimental results are listed in the last column. For CuCl and CuBr the binding energies can be estimated from Eq. (2.15) and are seen to be in excellent agreement with experiment as has been noted by others.[3,15] In $Cu_2O$ the electron mass and dielectric constant have been determined to be $m_e^* = 0.61m$ and $\epsilon_0 = 7.1$.[28] Using the exciton binding energy of the green series we estimate an effective hole mass from the usual hydrogenic formula to be $m_h = 6.0m$, leading to the value $\sigma = 0.1$. listed in Table IV. The calculated molecular binding energy is 16 meV. Gross and Kreingold[7(a)] identified a series of lines with the decay of the excitonic molecule and determined a binding energy of 18.5 meV. However, recent work by Petroff *et al.*[7(b)] appears to indicate that this assignment is incorrect. In the yellow series the hole mass is known to be $m_h = 0.84m$,[28] giving $\sigma = 0.73$ and a molecular binding energy of 3.3 meV. This state has not been observed.

The calculations including anisotropy of the heavy mass are most relevant to the question of excitonic molecules in the hexagonal group-II-VI compounds. In these materials the electron mass is light and essentially isotropic while the hole mass is approximately a factor of 5 heavier, with the mass parallel to the $c$ axis much larger than the transverse mass[29] (in the discussion presented here we will ignore the difference in the transverse and longitudinal dielectric constants since it is relatively small).[29] There is a difficulty in directly applying the results of the present paper to these compounds because of the rather strong exchange interaction between the electron and the hole.[30,31] When the $\Gamma_9$ valence band is highest the excitons form two doublets of $\Gamma_5$ and $\Gamma_6$ symmetry with the $\Gamma_6$ level lowest. The splitting between these levels is directly proportional to the electron-hole exchange interaction in the limit that this interaction is small compared to the axial crystal field. In CdS the splitting is 1.3 meV and becomes smaller as the excitonic wave function becomes more extended. In order to crudely estimate the effect of the electron-hole exchange interaction on the molecular binding energy, we argue as follows. In the molecule we pair the two-electron spins together to form a singlet. Similarly the hole spins are paired to form a singlet state. (For the holes the spin referred to here is a pseudo-spin-variable used to label the two states of the $\Gamma_9$ doublet.[30]) Regarding the molecule as two essentially separate excitons, each exciton in the above state finds itself 50% of the time in a $\Gamma_5$ state and 50% in a $\Gamma_6$ state. Therefore, such a configuration would be raised in energy by an amount equal to the exchange splitting between $\Gamma_5$ and $\Gamma_6$. This is undoubtedly an overestimate of

TABLE IV. Mass ratio, exciton binding energy, calculated molecular binding energies, and observed molecular binding energies for three copper compounds. All energies are in meV. References to the experimental papers are contained in the text. In $Cu_2O$ the observation is uncertain [Ref. 7(b)].

| | $\sigma$ | $E_x$ | $E_B$(calc) | $E_B$(expt) |
|---|---|---|---|---|
| CuBr | 0.01 | 110 | 29 | 29 |
| CuCl | 0.02 | 190 | 44 | 44 |
| $Cu_2O$ (green series) | 0.10 | 150 | 16 | 18.5 |
| $Cu_2O$ (yellow series) | 0.73 | 97 | 3.3 | ··· |

the effect of the electron-hole exchange since, in fact, it is expected to be a short-range interaction,[32] important only when the electron and hole are near each other, and should not tend to depair the electrons in the region where they exchange places. In Table V we have listed the masses, exciton binding energies, and the molecular binding energies for CdS,[30] CdSe,[33] and ZnS.[29,34] We also list there the $\Gamma_5$-$\Gamma_6$ splitting[31] as it is not taken into account in the listed molecular binding energies. The binding energies are quite small. It appears that CdSe presents the best possibility for observing excitonic molecules in this series of compounds. Another effect not included here is possible virtual admixture of other exciton states arising from the $B$ and $C$ series. Admixtures of these states would enhance the binding energy. They may be important in ZnO, where the upper two valence bands are quite close in energy.

Finally, there has been considerable speculation regarding excitonic molecules in Si and Ge.[15] Although it is clear that the original observations[8] ascribed to molecules are actually associated with electron-hole drops,[9] it is of interest to ask whether some molecular state could compete with the metallic state and whether molecules could form at low temperatures and densities. In Ge the masses of the electrons and holes appropriate for calculating the exciton binding energies are almost equal. Even though the electron mass is quite anisotropic with $m_{e\parallel}/m_{e\perp}=0.052$, this anisotropy is not sufficient to enhance the molecular binding energy appreciably, as can be seen from the results in Fig. 4. Therefore, we expect molecules to have a binding energy of no more than a few percent of the exciton energy ~ 0.1 meV and that the molecular-type state cannot compete favorably with the metallic state.[10-12] In Si the bands are more isotropic[11,12] and consequently the binding energy will be approximately $\sim 0.03E_x^0$ (= 0.24 meV), again a very small energy. Recently Wang and Kittel[35] have suggested that larger complexes of excitons than the simple biexciton molecule are stable in Ge and Si. These authors took the hole mass to be infinite and, therefore, not only have much larger binding energies but also have no effects from the orthogonality conditions on the holes. Since the typical masses of the electrons and holes in Ge and Si are approximately equal, the most important exclusion principle effect is that for the holes. Except in the singlet state of the molecule, the exclusion principle leads to strongly repulsive interactions[12] and inhibits binding. Therefore, we question the conclusions of Wang and Kittel[35] that such higher complexes are more stable than the biexciton in Ge and Si.

TABLE V. Various mass parameters, exciton binding energies, and predicted molecular binding energy. Energies are in meV. $E_{\Gamma_5}-E_{\Gamma_6}$ splitting is also listed since some fraction of this energy must be subtracted from the energies as discussed in text. References for the experimental numbers are given in the text.

| | CdS | CdSe | ZnS |
|---|---|---|---|
| $m_e$ | 0.205 | 0.13 | 0.28 |
| $m_{h\parallel}$ | 5.0 | 2.5 | 1.4 |
| $m_{h\perp}$ | 0.7 | 0.45 | 0.49 |
| $\sigma$ | 0.21 | 0.13 | 0.175 |
| $\gamma$ | 0.14 | 0.18 | 0.35 |
| $E_x^B$ | 27 | 15 | 36 |
| $E_M^B$ | 2 | 1.5 | 2.8 |
| $E_{\Gamma_5}-E_{\Gamma_6}$ | 1.3 | 0.2 | 2.0 |

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## APPENDIX A: HOLE KINETIC ENERGY

We will calculate the contribution of the hole kinetic energy to the effective potential $U_\sigma(R)$. Consider a wave function of the form

$$\psi\equiv\psi(P,T)\ ,$$
$$P=r_{1a}+r_{1b}+r_{2a}+r_{2b}\ , \tag{A1}$$
$$T=r_{1a}-r_{1b}-r_{2a}+r_{2b}\ .$$

Then

$$\vec{\nabla}_a\psi=\frac{\partial\psi}{\partial P}\,\vec{\nabla}_aP+\frac{\partial\psi}{\partial T}\,\vec{\nabla}_aT$$

and

$$\nabla_a^2\psi=\frac{\partial^2\psi}{\partial P^2}\,(\vec{\nabla}_aP)^2+\frac{\partial\psi}{\partial P}\,\nabla_a^2P+\frac{2\partial^2\psi}{\partial P\partial T}\,(\vec{\nabla}_aP\cdot\vec{\nabla}_aT)$$
$$+\frac{\partial^2\psi}{\partial P^2}\,(\vec{\nabla}_aT)^2+\frac{\partial\psi}{\partial T}\,\nabla_a^2T\ .$$

Therefore,

$$(\nabla_a^2+\nabla_b^2)\psi=\frac{\partial^2\psi}{\partial P^2}\,[(\vec{\nabla}_aP)^2+(\vec{\nabla}_bP)^2]+\frac{\partial\psi}{\partial P}[\nabla_a^2P+\nabla_b^2P]$$
$$+\frac{2\partial^2\psi}{\partial P\partial T}\,[(\vec{\nabla}_aP)\cdot(\vec{\nabla}_aT)+(\vec{\nabla}_bP)\cdot(\vec{\nabla}_bT)]$$
$$+\frac{\partial^2\psi}{\partial T^2}\,[(\vec{\nabla}_aT)^2+(\vec{\nabla}_bT)^2]+\frac{\partial\psi}{\partial T}\,[\nabla_a^2T+\nabla_b^2T]\ . \tag{A2}$$

But from (A1),

$$\vec{\nabla}_aP=\vec{\nabla}_ar_{1a}+\vec{\nabla}_ar_{2a}$$

$$= -\hat{r}_{1a} - \hat{r}_{2a} \;,$$

$$\vec{\nabla}_a T = \vec{\nabla}_a r_{1a} - \vec{\nabla}_a r_{2a}$$

$$= -\hat{r}_{1a} + \hat{r}_{2a} \;,$$

where $\hat{r}_{1a}$ are unit vectors in the $\vec{\mathrm{r}}_{1a}$ direction, and

$$\nabla_a^2 P = 2(r_{1a}^{-1} + r_{2a}^{-1}) \;, \quad \nabla_a^2 T = 2(r_{1a}^{-1} - r_{2a}^{-1}) \;.$$

Therefore we have

$$(\vec{\nabla}_a P)^2 + (\vec{\nabla}_b P)^2 = 4 + 2(\hat{r}_{1a}\cdot\hat{r}_{2a} + \hat{r}_{1b}\cdot\hat{r}_{2b}), \tag{A3a}$$

$$(\vec{\nabla}_a T)^2 + (\vec{\nabla}_b T)^2 = 4 - 2(\hat{r}_{1a}\cdot\hat{r}_{2a} + \hat{r}_{1b}\cdot\hat{r}_{2b}), \tag{A3b}$$

$$\nabla_a^2 P + \nabla_b^2 P = 2(r_{1a}^{-1} + r_{2a}^{-1} + r_{1b}^{-1} + r_{2b}^{-1}), \tag{A3c}$$

$$\nabla_a^2 T + \nabla_b^2 T = 2(r_{1a}^{-1} - r_{2a}^{-1} - r_{1b}^{-1} + r_{2b}^{-1}). \tag{A3d}$$

But

$$(\vec{\nabla}_a T)\cdot(\vec{\nabla}_a P) + (\vec{\nabla}_b T)\cdot(\vec{\nabla}_b P)$$
$$= (\vec{\nabla}_a r_{1a})^2 - (\vec{\nabla}_a r_{2a})^2 - (\vec{\nabla}_b r_{1b})^2 + (\vec{\nabla}_b r_{2b})^2 = 0 \;.$$

Note that (A3c) and (A3d) are invariant with respect to interchange of the holes and electrons while (A3a) and (A3b) are not. We use this fact to write

$$(\nabla_a^2 + \nabla_b^2)\psi = (\nabla_1^2 + \nabla_2^2)\psi + 2\left(\frac{\partial^2\psi}{\partial P^2} - \frac{\partial^2\psi}{\partial T^2}\right)$$
$$\times(\hat{r}_{1a}\cdot\hat{r}_{2a} + \hat{r}_{1b}\cdot\hat{r}_{2b} - \hat{r}_{1a}\cdot\hat{r}_{1b} - \hat{r}_{2a}\cdot\hat{r}_{2b}) \;,$$

i.e., for the form of $\psi$ used,

$$(\nabla_a^2 + \nabla_b^2)\psi = (\nabla_1^2 + \nabla_2^2)\psi - \tfrac{1}{2}k^2(1-\beta^2)$$
$$\times(\hat{r}_{1a} - \hat{r}_{2b})\cdot(\hat{r}_{1b} - \hat{r}_{2a})\psi \;.$$

Using the definitions of $s_1$, $s_2$, $t_1$, and $t_2$ given in Eq. (2.8) in the text, we can write

$$\hat{r}_{1a}\cdot\hat{r}_{1b} = \frac{s_1^2 + t_1^2 - 2\bar{R}^2}{s_1^2 - t_1^2} \;,$$

$$\hat{r}_{1a}\cdot\hat{r}_{2a} = \frac{s_1 t_1 s_2 t_2}{2(s_1+t_1)(s_2+t_2)} - \frac{s_1 t_1 + s_2 t_2}{(s_1+t_1)(s_2+t_2)} + \bar{R}^2 \;, \tag{A4}$$

where $\bar{R} = kR$. The integrals are then tedious but straightforward; we will just quote the results

$$I_1 \equiv \int \hat{r}_{1a}\cdot\hat{r}_{2a}\psi^2 d^3r_1 d^3r_2 / S^2(R)$$
$$= [(\bar{R}+1)^2\bar{R}^2(y_2 - y_0)^2 e^{-2\bar{R}}$$
$$- 4(\bar{R}+1)^2 y_1^2 + \tfrac{32}{9}\bar{R}^2(\bar{R}+1)^2][1/S^2(R)]$$

and

$$I_2 \equiv \int \frac{\hat{r}_{1a}\cdot\hat{r}_{1b}\psi^2 d^3r_1 d^3r_2}{S^2(R)}$$
$$= \frac{2e^{-2\bar{R}}}{S^2(R)}[(\bar{R}+1)^2 y_0^2 - \tfrac{1}{4}\bar{R}^4(y_0 - y_2)^2] \;,$$

where we have used Nordsieck's notation on the right-hand side of the equations

$$y_n = \frac{\partial^n}{\partial B^n}\,\frac{\sinh B}{B} \;; \quad B = \beta\bar{R} \;.$$

As a check it was found that $\int d^3R S^2(R)(I_1 - I_2) = 0$ which shows that this term is zero in the Hylleraas-Ore[1] calculation.[19]

## APPENDIX B: LARGE-*R* EXPANSION OF INTERACTION TERM

In this appendix we wish to evaluate the electron-electron interaction energy in the limit of large hole separations. In particular we have to evaluate the integral

$$I(R) = \frac{1}{S^2(R)}\int d^3r_1\, d^3r_2\, \frac{e^2}{r_{12}}\,\psi^2(r_1, r_2, R) \;, \tag{B1}$$

where

$$\psi = 2\exp[-\tfrac{1}{2}k(r_{1a} + r_{2a} + r_{1b} + r_{2b})]$$
$$\times \cosh\tfrac{1}{2}\beta k(r_{1a} - r_{1b} - r_{2a} + r_{2b}) \;,$$

$S(R)$ is the normalization integral, and $R$ is the hole separation. In this appendix we set $k=1$, since the $k$ variable simply sets the scale of length. For large $R$ the dominant terms are $r_{1b}$, $r_{2a} \approx R$, and $r_{1a}$, $r_{2b} \ll R$ or $r_{1a}$, $r_{2b} \approx R$ and $r_{1b}$, $r_{2a} \ll R$. Both cases give identical contributions and it is sufficient to examine the former when we have

$$\vec{\mathrm{r}}_{1b} = \vec{\mathrm{R}}_{ab} + \vec{\mathrm{r}}_{1a} \;, \quad \vec{\mathrm{r}}_{2a} = -\vec{\mathrm{R}}_{ab} + \vec{\mathrm{r}}_{2b} \;,$$
$$\vec{\mathrm{r}}_{12} = \vec{\mathrm{R}}_{ab} + \vec{\mathrm{r}}_{1a} - \vec{\mathrm{r}}_{2b} \;.$$

Then,

$$r_{12} = R\left(1 + 2\,\frac{(\vec{\mathrm{r}}_{1a} - \vec{\mathrm{r}}_{2b})\cdot\vec{\mathrm{R}}_{ab}}{R^2} + \frac{(\vec{\mathrm{r}}_{1a} - \vec{\mathrm{r}}_{2b})^2}{R^2}\right)^{1/2} \;.$$

Expanding the square root we get

$$I = \frac{e^2}{R} - \frac{e^2}{R}\int d^3r_1\, d^3r_2\, \frac{\psi^2}{S^2(R)}\,\frac{(\vec{\mathrm{r}}_{1a} - \vec{\mathrm{r}}_{2b})\cdot\vec{\mathrm{R}}_{ab}}{R^2}$$
$$+ \frac{e^2}{R}\int d^3r_1\, d^3r_2\, \frac{\psi^2}{S^2(R)}\left(-\frac{(\vec{\mathrm{r}}_{1a} - \vec{\mathrm{r}}_{2b})^2}{2R^2} + \frac{3[(\vec{\mathrm{r}}_{1a} - \vec{\mathrm{r}}_{2b})\cdot\vec{\mathrm{R}}_{ab}]^2}{2R^4}\right) \equiv \frac{e^2}{R}(1 + I_a + I_b) \;.$$

Since $\beta^2 \approx 0.5$ we need only consider the dominant terms:

$$\psi^2 = e^{-(1+\beta)(r_{1a}+r_{2b})} e^{-(1-\beta)(r_{1b}+r_{2a})}$$

$$= e^{-(1+\beta)(r_{1a}+r_{2b})} \exp\left[-(1-\beta)\left(2R + \frac{(\vec{r}_{1a}-\vec{r}_{2b})\cdot\vec{R}_{ab}}{R} + \frac{1}{2}\,\frac{r_{1a}^2+r_{2b}^2}{R} - \frac{(\vec{r}_{1a}\cdot\vec{R}_{ab})^2+(\vec{r}_{2b}\cdot\vec{R}_{ab})^2}{2R^3}\right)\right] + \cdots ,$$

$$I_a = -\frac{1}{S^2(R)R^2}\, e^{-2(1-\beta)R} \int d^3r_1\, d^3r_2\, \exp[-(1+\beta)(r_{1a}+r_{2b})]$$

$$\times \exp[-(1-\beta)(\vec{r}_{1a}-\vec{r}_{2b})\cdot\vec{R}_{ab}/R]\,(\vec{r}_{1a}-\vec{r}_{2b})\cdot\vec{R}_{ab}\left[1-(1-\beta)\left(\frac{r_{1a}^2+r_{2b}^2}{2R} - \frac{(\vec{r}_{1a}\cdot\vec{R}_{ab})^2+(\vec{r}_{2b}\cdot\vec{R}_{ab})^2}{2R^3}\right)\right] .$$

We will measure $r_1$ from $a$, $r_2$ from $b$, and use polar coordinates, the $z$ axis being given by $\vec{R}_{ab}$. Thus,

$$I_a = -\frac{1}{R^2}\,\frac{e^{-2(1-\beta)R}}{S^2(R)} \int_0^\infty r_1^2 dr_1\, r_2^2\, dr_2 \int_{-1}^{1} d\mu_1\, d\mu_2\, e^{-(1+\beta)(r_1+r_2)}\, e^{-(1-\beta)(r_1\mu_1-r_2\mu_2)}$$

$$\times R(r_1\mu_1 - r_2\mu_2)\left[1-(1-\beta)\left(\frac{r_1^2+r_2^2}{2R} - \frac{r_1^2\mu_1^2+r_2^2\mu_2^2}{2R}\right)\right].$$

After rearranging, this can be written

$$I_a = -\frac{1}{RS^2(R)}\, e^{-2(1-\beta)R} \times\left(2I_1I_2 - \frac{(1-\beta)I_1I_3}{R} - \frac{(1-\beta)I_4I_2}{R}\right) , \qquad \text{(B2)}$$

where

$$I_1 = \int_0^\infty dr_1 r_1^2\, e^{-(1+\beta)r_1} \int_{-1}^{1} d\mu_1 e^{-(1-\beta)r_1\mu_1} \times 1 ,$$

$$I_2 = \int_0^\infty dr_1 r_1^2\, e^{-(1+\beta)r_1} \int_{-1}^{1} d\mu_1 e^{-(1-\beta)r_1\mu_1} \times r_1\mu_1 ,$$

$$I_3 = \int_0^\infty dr_1 r_1^2\, e^{-(1+\beta)r_1} \int_{-1}^{1} d\mu_1 e^{-(1-\beta)r_1\mu_1} \times r_1^3(1-\mu_1^2)\mu_1 , \qquad \text{(B3)}$$

$$I_4 = \int_0^\infty dr_1 r_1^2 e^{-(1+\beta)r_1} \int_{-1}^{1} d\mu_1 e^{-(1-\beta)r_1\mu_1} \times r_1^2(1-\mu_1^2) ,$$

$$I_5 = \int_0^\infty dr_1 r_1^2 e^{-(1+\beta)r_1} \int_{-1}^{1} d\mu_1 e^{-(1-\beta)r_1\mu_1} \times r_1^2(1-3\mu_1^2) .$$

$I_b$ is given a similar analysis. We get

$$I_b = \frac{e^{-2(1-\beta)R}}{2R^2S^2(R)}\,(-2I_5I_1 + 4I_2^2) . \qquad \text{(B4)}$$

The evaluation of the integrals $I_1$–$I_5$ is straightforward and we will only quote the results:

$$I_1 = \frac{(1+\beta)}{4\beta^2} ; \qquad I_2 = \frac{(1-\beta^2)}{4\beta^3} ;$$

$$I_3 = -\frac{3}{4\beta^4}(1-\beta^2) ; \quad I_4 = \frac{1+\beta}{2\beta^3} ;$$

$$I_5 = -\frac{3(1-\beta^2)(1-\beta)}{4\beta^4} .$$

We also need the large-$R$ expansion of $S^2(R)$ which is again straightforward:

$$S^2(R) = e^{-(1-\beta)2R}\left(I_1^2 - \frac{(1-\beta)I_4I_1}{R}\right)$$

$$= e^{-(1-\beta)2R}\left(\frac{(1+\beta)^2}{16\beta^4} - \frac{(1+\beta)^2(1-\beta)}{8\beta^5 R}\cdots\right) .$$

Finally, collecting all the terms together we get

$$I(R) = \frac{e^2}{R}\left(1 + \frac{2(1-\beta)}{\beta R} + \frac{4(1-\beta)^2}{\beta^2R^2}\right) .$$

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*Permanent address: Department of Applied Physics, Stanford University, Stanford, Calif. 94305.

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# Energy-Level Spectra of Electrons at the (111), (110), and (100) Surfaces of Silicon and Germanium by Ion-Neutralization Spectroscopy

H. D. Hagstrum and G. E. Becker
*Bell Laboratories, Murray Hill, New Jersey 07974*

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Energy-level spectra obtained for the (111), (110), and (100) faces of Si and Ge by ion-neutralization spectroscopy (INS) bear only a superficial resemblance to the bulk density of states for these solids. In particular, the energies of small peaks in the INS-unfold function vary from one surface to another, and also differ from the energies of bulk critical points determined either by theory or by spectroscopies which more nearly yield bulk properties. A similar statement can be made for the width of the degenerate $p$ band, which is narrower at the surface as revealed by INS than it is in the bulk. Thus, the principal conclusion of this paper is that the local density of states (density of states weighted by local-wave-function magnitude) is significantly modulated as one proceeds from the bulk of a solid to its surface. The surface state observed for Si(111) by photoemission as overlapping the top of the valence band is seen in the INS spectra for both the Si(111)1 and Si(111)7 surfaces. The INS spectra for other Si surfaces and for all of the Ge surfaces studied do not show the kind of definitive evidence for a surface state seen in the Si(111) data although we cannot say that such surface states are not present with reduced intensity.

## I. INTRODUCTION

The method of ion-neutralization spectroscopy (INS) has been used to determine energy-level spectra of several surfaces each of silicon and germanium. This is the first use of this spectroscopic method in the study of the surfaces of the elemental semiconductors. It is found that the energy-level structures at the various surfaces reflect the gross features of the bulk energy-level structure but differ considerably in detail both from the bulk and among themselves. In particular, what appear to be critical points at the surfaces as indicated by peaks in the INS transition-density functions are found to differ in energy from surface to surface and from bulk critical points predicted by theory[1-4] or observed by other electron spectroscopies.[5-8] Demonstration of this surface modification of bulk band structure depends directly upon the high degree of surface specificity of the INS.

Filled surface states are also in evidence on some of the surfaces studied. On the Si(111)7 and Si(111)1 surfaces, there is evidence for a state which is centered a fraction of a volt below the valence-band edge, and which is not easily identified as a surface-shifted bulk critical point. This state lies close to the position of the state observed by photoemission[9,10] on the cleaved Si(111) face and identified as a surface state. The INS data for other surfaces do not show evidence for such a state of comparable magnitude although a state could well be present at an intensity which makes it not readily distinguishable from other features of the surface local density of states.

The first studies of the ion-neutralization pro-