Trion ground-state energy: Simple results

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We investigate the trion binding energy in a three-dimensional semiconductor, with bare Coulomb interaction between charges and effective mass approximation for the electron and hole dispersion relations. This is done by making use of a previously proposed exact method for the three-body problem. The calculations cover the complete range of electron-to-hole mass ratio. We find perfect agreement with existing variational calculations. Investigating the small- and large-mass-ratio regimes, we build a three-parameter interpolating formula for the trion binding energy $E_b(r)$ in terms of the exciton binding energy, where r is the electron to exciton mass ratio. This formula, $E_b(r) = 0.71347 - 0.11527\, r - 0.18580\, \sqrt{1-r}$, in atomic units, is in full agreement, within our precision, with our numerical results over the complete range of mass ratio.

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I. INTRODUCTION

Optical properties of semiconductors, mostly in quantum wells and in reduced dimensions, are, to a large extent, controlled by their few-body low-energy excitations [1]. The most important is the exciton, but trions and biexcitons are also quite relevant. Following the prediction of its existence [2] and its observation [3,4], the trion (or "charged exciton") has, indeed, been recognized as an important ingredient in understanding optical properties. In quantum wells the trion may arise, for example, from electrons forming bound states with photocreated excitons. The extra electron may come from intentional doping and also from impurities. In addition to quantum wells, the trion is also important in understanding the optical properties of quite interesting materials which have been the subject of a number of recent investigations, such as nanowires [5], carbon nanotubes [6], and transition-metal dichalcogenides [7–11]. In this last case detailed calculations on a material-realistic footing have been, in particular, performed for monolayers including various substrate effects [12,13].

It is naturally quite important to know the binding energy of all the excitations in order to identify them properly and ultimately manipulate the optical properties. While in many cases this is achieved for the exciton, the case of the trion is more difficult. Indeed, if there are not enough of them, due, for example, to low doping, the trion line is too weak to be seen. On the other hand, in the case of high doping, the trion linewidth gets large, which makes it difficult to identify. Moreover, in this case the presence of an electronic Fermi sea makes the trion problem even more difficult due, in particular, to Pauli blocking effects [10,14,15]. The matter is complicated enough to make the identification of the trion line controversial [16]. Since the identification of the trion line is not obvious, precise calculations of its position are clearly of interest to provide an additional ingredient for the identification.

In a recent paper [17] we proposed a general, exact, and efficient method for handling the three-body problem, with the aim to apply it to the trion [18]. The essential idea of this method is to make full use of the solution of the two-body problem, corresponding to the exciton, to solve the trion problem. The solution of the two-body problem comes in practice through the knowledge of the corresponding T matrix. This approach is of general interest since the trion problem is not an easy one, and it is often simplified in order to achieve an effective solution. Our method leads to solving a simple integral equation, a task, in principle, easier than what has to be done with more sophisticated methods. This is at least an alternative method of calculation for trion properties, which can complement other approaches.

Let us stress that the interest of our method is not restricted to the case where the electron-hole Hamiltonian corresponds to the effective mass approximation, which we will use here, nor to the three-dimensional case we will consider. Indeed, it can be applied, in principle, to any situation, for example, quantum wells, two-dimensional (2D) systems [7–11], and embedded quasi-2D systems [19], where the electron and hole dynamics is more complicated. Similarly, it is not restricted to the bare Coulomb interaction, and there is, in principle, no problem with taking screening into account and using, for example, the Rytova-Keldysh potential [20]. All this makes the calculation of the exciton properties more involved. However, the point is that, as soon as the exciton is known through its T matrix, the trion energy can be calculated within exactly the same framework. This ensures that the trion properties are obtained within exactly the same theoretical description as the exciton properties, avoiding any incoherence which might arise from practical problems when the two objects are handled independently. Another quite important interest of the method is that it provides, at the same time as the binding energy, the trion wave function, although we will not make use of it in the present paper. Finally, its formalism is well suited for extensions to many-body problems, such as the trion in the presence of the electronic Fermi sea.

We have applied [17] our method to the specific case of the helium atom ground state to check its validity and efficiency.

In this specific case, since we have to deal with the Coulomb interaction, we have used the very convenient expression for the T matrix obtained by Schwinger [21], which is almost analytical, even if it is somewhat singular. This check on the helium case has been completely satisfactory. However, it must be mentioned that, in retrospect, this check was dealing with a fairly easy situation. Indeed, in the helium case, the repulsive interaction between the two electrons is fairly weak compared to the attractive interaction between the nucleus and the two electrons. Actually, a perturbative calculation gives already an approximate result which is not too bad. Naturally, our calculation has been an exact one, dealing with the full three-body problem. But the conditions were good, and the numerical implementation could go quite smoothly.

Here we want to use this method to actually calculate the trion binding energy. As a first case, we will deal with the situation which is formally the simplest one, namely, the three-dimensional case within the effective mass approximation for electron and hole. The interaction is the bare Coulomb interaction, so we can again use Schwinger's T matrix. This case has already been investigated [14,22], so we can compare our results to existing work. Our aim is to investigate the effect of the electron-hole mass ratio and see how important it is. Despite its apparent simplicity this case turns out to be a fairly stringent test of our method because the trion is quite weakly bound with respect to the exciton. Very roughly speaking the trion and the exciton are almost degenerate. Clearly, such a situation leads to complications, which are probably present whatever the method used to solve the problem. As we will see, this physical situation indeed makes our calculations, in practice, somewhat more complicated than in the helium case.

In most compounds the electronic effective mass m_e is lighter or of the order of the hole mass m_h, so in the standard negatively charged trion, with two electrons and one hole, corresponding to the (eeh) or (X^-) situation, the mass ratio m_e/m_h is smaller than unity or of the same order. However, there is also the possibility of a positively charged trion, with two holes and one electron corresponding to the (ehh) or (X^+) situation. Nevertheless, this second case is formally identical to the first one, provided we exchange the roles of electrons and holes. Accordingly, it corresponds to the case where the mass ratio m_e/m_h is larger than unity. Hence, dealing with the general situation is equivalent to studying the (eeh) trion with a mass ratio having any value.

We will pay particular attention to the limiting domains where this mass ratio is either small or large. These correspond to the cases where the trion is physically similar to the negatively charged hydrogen ion H^- or to the positively charged hydrogen molecule $H_2{}^+$. It is in these regimes that the dependence of the trion binding energy on the mass ratio is stronger. In between the binding energy has a minimum, and the domain where it takes values near this minimum is fairly extended. As a result the trion binding energy is very weakly dependent on the mass ratio in a wide domain, a fairly surprising physical feature. Hence, an understanding of the binding energy in the limiting domains of small and large mass ratios leads to a better grasp of the physical situation in between. Elaborating quantitatively on this principle, we have, in addition, built a simple interpolation formula which describes properly the behavior of the binding energy in these two limiting regimes. Very surprisingly, this formula happens to be in perfect agreement with our numerical results in the whole range of mass ratio. The agreement is so good that, for any practical purpose, there is no need of further numerical calculations to have, in this physical situation, the binding energy for any mass ratio, as if we had an analytical result.

In the next section we summarize our formalism and discuss its implementation. The following section considers the limiting domains of low and high mass ratios. We then give our results for the binding energy, compare them to the literature, and provide our interpolation formula. The paper closes with a summary.

II. FORMALISM

The approach we used in [17] is a diagrammatic approach. It makes full use of the solution of the two-body problem since a basic ingredient is the T matrix corresponding to this problem. In the case of the Coulomb interaction this T_2 matrix has a quite simple form found by Schwinger [21]. From this knowledge an integral equation for the scattering amplitude T_3 of an electron on the exciton is obtained. Basically, the energy spectrum of the trion, and more specifically, its ground-state energy, is found from the poles of this scattering amplitude T_3. Actually, in order to find the information we are looking for we need [17] to consider only the on-the-shell expression for T_3. More specifically, we need a symmetrized (corresponding to the electronic singlet expected for the trion ground state) amplitude $T(\mathbf{p},\mathbf{p}')$, where $\mathbf{p}$ and $\mathbf{p}'$ are the momenta of the $\uparrow$ and $\downarrow$ electron spin, respectively. Moreover, we need an analogous amplitude $S(\mathbf{Q},\mathbf{q})$ for electron-hole scattering. Naturally, the whole problem is solved in the center-of-mass reference frame, so that the total momentum is zero.

We have found [17] that, for $E>0$ to be the trion binding energy, $T(\mathbf{p},\mathbf{p}')$ and $S(\mathbf{Q},\mathbf{q})$ must satisfy the following homogeneous linear integral equations:

$$T(\mathbf{p},\mathbf{p}') = -\frac{1}{E+\frac{\mathbf{p}^2+\mathbf{p}'^2}{2m_e}+\frac{(\mathbf{p}+\mathbf{p}')^2}{2m_h}}\sum_{\mathbf{k}}\left[T_2\left(\left\{-E-\frac{\mathbf{p}'^2}{2m_e},-\mathbf{p}'\right\};\mathbf{p}+r\mathbf{p}',\mathbf{k}+r\mathbf{p}'\right)T(\mathbf{p}',\mathbf{k})\right.$$
$$\left.+T_2^e\left(\left\{-E-\frac{(\mathbf{p}+\mathbf{p}')^2}{2m_h},\mathbf{p}+\mathbf{p}'\right\};\frac{\mathbf{p}-\mathbf{p}'}{2},\mathbf{k}\right)S(\mathbf{p}+\mathbf{p}',\mathbf{k})\right], \quad (1)$$

$$S(\mathbf{Q},\mathbf{q}) = -\frac{1}{E+\frac{\mathbf{Q}^2}{2m_h}+\frac{\mathbf{Q}^2+4\mathbf{q}^2}{4m_e}}$$
$$\times\sum_{\mathbf{k}}T_2\left(\left\{-E-\frac{\left(\frac{\mathbf{Q}}{2}+\mathbf{q}\right)^2}{2m_e},-\left(\frac{\mathbf{Q}}{2}+\mathbf{q}\right)\right\};\left(\frac{\mathbf{Q}}{2}-\mathbf{q}\right)+r\left(\frac{\mathbf{Q}}{2}+\mathbf{q}\right),\mathbf{k}+r\left(\frac{\mathbf{Q}}{2}+\mathbf{q}\right)\right)T\left(\frac{\mathbf{Q}}{2}+\mathbf{q},\mathbf{k}\right)+(\mathbf{q}\leftrightarrow-\mathbf{q}). \quad (2)$$

Here m_e and m_h are the electron and hole mass, respectively, and $r = m_e/M$ is the ratio between the electron mass and the exciton total mass $M = m_e + m_h$. $T_2(P; \mathbf{k}, \mathbf{k}') = T_2(\omega, \mathbf{k}, \mathbf{k}')$ is the electron-hole T_2 matrix, where $P = \{\Omega, \mathbf{P}\}$ is an energy-momentum four-vector and $\omega = \Omega - \mathbf{P}^2/2M$. Similarly, T_2^e is the T_2 matrix for the propagation of an electron pair (and here the total mass is $M' = m_e + m_e = 2m_e$). The specific expressions resulting from the Schwinger $T_2(\omega, \mathbf{k}, \mathbf{k}')$ are given below.

It is convenient to rewrite these equations with reduced units, taking $a_0 = 4\pi\epsilon/(2\mu_{eh}e^2)$ as the unit of length, with ϵ being the medium permittivity and $\mu_{eh} = m_e m_h/(m_e + m_h)$ being the reduced exciton mass. Similarly, we take $1/a_0$ as the unit wave vector and $1/(2\mu_{eh}a_0^2)$ as the energy unit (this is twice the usual atomic unit). In this way, with $K^2 = 2\mu_{eh}a_0^2 E$, Eqs. (1) and (2) become, with all wave vectors now being in reduced units,

$$t(\mathbf{p}, \mathbf{p}') = -\frac{1}{K^2+(1-r)(\mathbf{p}^2+\mathbf{p}'^2)+r(\mathbf{p}+\mathbf{p}')^2} \int \frac{d\mathbf{k}}{(2\pi)^3} \left[t_2(\kappa, \mathbf{p}+r\mathbf{p}', \mathbf{k}+r\mathbf{p}')\, t(\mathbf{p}', \mathbf{k}) + t_2^e\left(\kappa_e, \frac{\mathbf{p}_-}{2}, \mathbf{k}\right) s(\mathbf{p}_+, \mathbf{k}) \right], \tag{3}$$

$$s(\mathbf{Q}, \mathbf{q}) = -\frac{2}{2K^2+(1+r)\mathbf{Q}^2+4(1-r)\mathbf{q}^2} \int \frac{d\mathbf{k}}{(2\pi)^3}\, t_2(\kappa_Q, \mathbf{Q}_-+r\mathbf{Q}_+, \mathbf{k}+r\mathbf{Q}_+)\, t(\mathbf{Q}_+, \mathbf{k}) + (\mathbf{q} \leftrightarrow -\mathbf{q}), \tag{4}$$

where we have used the abbreviations $\mathbf{p}_\pm = \mathbf{p} \pm \mathbf{p}'$, $\mathbf{Q}_\pm = \mathbf{Q}/2 \pm \mathbf{q}$, $\kappa = [K^2 + (1-r^2)\mathbf{p}'^2]^{1/2}$, $\kappa_Q = [K^2 + (1-r^2)\mathbf{Q}_+^2]^{1/2}$, and $\kappa_e = [(1-r)K^2/2 + (1-r^2)\mathbf{p}_+^2/4]^{1/2}$ and we have for t_2 and t_2^e the explicit expressions

$$t_2(\kappa, \mathbf{q}, \mathbf{q}') = -\frac{4\pi z}{(\mathbf{q}-\mathbf{q}')^2} \int_0^1 du\, \frac{u^{-\frac{1}{2\kappa}}(1-u^2)}{[u+z(1-u)^2]^2},$$

$$t_2^e(\kappa_e, \mathbf{q}, \mathbf{q}') = \frac{4\pi z_e}{(\mathbf{q}-\mathbf{q}')^2} \int_0^1 du\, \frac{u^{\frac{1}{4\kappa_e}}(1-u^2)}{[u+z_e(1-u)^2]^2}, \tag{5}$$

with, in $t_2(\kappa, \mathbf{q}, \mathbf{q}')$, $z = (\kappa^2 + \mathbf{q}^2)(\kappa^2 + \mathbf{q}'^2)/[4\kappa^2(\mathbf{q}-\mathbf{q}')^2]$ and, in $t_2^e(\kappa_e, \mathbf{q}, \mathbf{q}')$, $z_e = (\kappa_{er}^2 + \mathbf{q}^2)(\kappa_{er}^2 + \mathbf{q}'^2)/[4\kappa_{er}^2(\mathbf{q}-\mathbf{q}')^2]$, with $\kappa_{er} = \kappa_e/(1-r)$. We note that the first term in the second equation for $s(\mathbf{Q}, \mathbf{q})$ is obtained merely from the first term in the first equation for $t(\mathbf{p}, \mathbf{p}')$ using the substitutions $\mathbf{p} \to \mathbf{Q}_-$ and $\mathbf{p}' \to \mathbf{Q}_+$.

The practical handling of these equations follows the same lines as those used in [17]. However, in practice the numerical work for the trion has turned out to be somewhat more complicated than for the helium case. The first problem comes from the iteration procedure we have followed to solve the coupled integral equations (3) and (4). Indeed, these equations can be understood as meaning that the linear operator corresponding to the right-hand side of these equations has an eigenvalue equal to 1, and for E to be the ground-state energy, it is easily seen [17] that this is the largest positive eigenvalue which must be equal to 1. In principle this largest eigenvalue can be found by merely iterating [17] the operator corresponding to the right-hand side.

However, this procedure converges efficiently only if the spectrum of this operator is well behaved. In looking for the trion ground state we have seen the appearance of complex eigenvalues with a large modulus, which totally spoil the iteration. Actually, this arises because we had treated the system of equations (5) as a 2×2 matrix. Fortunately, this problem has been completely solved by going to a 1×1 treatment, which eliminates the spurious complex eigenvalues. This is done by merely carrying the explicit expression for $s(\mathbf{Q}, \mathbf{q})$ given by Eq. (4) into Eq. (3). There is no problem in implementing this numerically, and the spurious complex eigenvalues disappear in this way.

Another problem we have found is the appearance of negative eigenvalues with large absolute values. However, one can, in principle, eliminate this kind of problem by shifting around the spectrum by linear transformations. If an operator A has a spectrum included in $[-a, b]$ (with $a, b > 0$), the operator $(A + a\mathbb{1})/(a + b)$ has its spectrum included in [0,1], so the largest eigenvalue can be obtained by iteration. Naturally, this slows down the convergence of the iteration, but we have found that this solves all our problems of this kind.

A more systematic problem is linked to the fact that the trion is weakly bound with respect to the exciton. If this relative binding were zero, with the trion binding equal to the exciton one, we would find cases where T_2 would diverge. Specifically, the exciton binding energy corresponds to $K = 1/2$, so for $\mathbf{p}' = 0$ we have $\kappa = 1/2$, and the integral for $t_2(\kappa, \mathbf{q}, \mathbf{q}')$ in Eq. (5) diverges. Naturally, the total trion binding energy is slightly larger than the exciton binding energy, and we are not in this singular situation. Nevertheless, we are near this singularity, and in practice this means that the corresponding integrals, while not being infinite, are much more sensitive to the values of the various parameters than in a standard situation. This automatically makes a precise numerical calculation more difficult to implement.

In particular, to avoid the u region responsible for the nearly divergent behavior, we have found it useful to avoid the low-u region (for example, the [0,0.5] domain) in the integral for $t_2(\kappa, \mathbf{q}, \mathbf{q}')$ in Eq. (5) by following Schwinger [21] and transforming it into a contour integral on a circle going around the origin $u = 0$. Writing this contour integral explicitly and skipping details, this amounts finally to writing

$$\int_0^{1/2} du\, f(u) = -\frac{1}{\sin\left(\frac{\pi}{2\kappa}\right)} \mathrm{Re}\left[e^{i\frac{\pi}{2\kappa}} \int_0^\pi d\theta\; u\, f(u) \right], \tag{6}$$

with $u = e^{i\theta}/2$ on the right-hand side integral. Here $f(u)$ is the integrand in the integral for $t_2(\kappa, \mathbf{q}, \mathbf{q}')$ in Eq. (5), which behaves as $u^{-1/2\kappa}$ when $u \to 0$. On the right-hand side the possible singular behavior for $\kappa \to 1/2$, for example, appears explicitly in the factor $\sin^{-1}[\pi/(2\kappa)]$. Note that one cannot extend this procedure to the whole [0,1] domain because one has to avoid possible contributions coming from poles of $f(u)$.

Finally, it is worth noticing that the case $r = 1$ is somewhat singular since divergences appear in some of the quantities

we have defined. This implies a specific treatment to remove these divergences. We have not proceeded to this treatment in the general case. However, it is of interest to consider the particular case where the two electrons are not interacting because our integral equations for this simpler problem can be fully solved analytically. Indeed, in this case we can ignore $s(\mathbf{Q},\mathbf{q})$ and set it to zero since it comes directly from the interaction between the two electrons. We are left with Eq. (3) for $t(\mathbf{p},\mathbf{p}')$, which becomes for $r=1$

$$t(\mathbf{p},\mathbf{p}') = -\frac{1}{K^2+(\mathbf{p}+\mathbf{p}')^2} \times \int \frac{d\mathbf{k}}{(2\pi)^3}\, t_2(K,\mathbf{p}+\mathbf{p}',\mathbf{k}+\mathbf{p}')\, t(\mathbf{p}',\mathbf{k}). \quad (7)$$

This equation is clearly compatible with a solution where $t(\mathbf{p},\mathbf{p}')=\tau(\mathbf{p}+\mathbf{p}')$ depends only on the single variable $\mathbf{p}+\mathbf{p}'$. This is actually simple to understand physically. The case $r=1$ corresponds to the situation where the two electrons are infinitely heavy and, in the absence of interaction between them, they interact only with the hole. It is physically fairly clear that the binding of the hole to the electrons will be the strongest if the two electrons are located at the same place. This is then just the problem of a single hole in the presence of a doubly charged electron. Hence, the binding energy is four times the exciton binding energy, that is, 4 Ry = 2 hartrees, which corresponds to $K=1$ with our reduced units. Since we deal only with the hole, it is natural to see only its momentum $\mathbf{p}_h$ appearing. But we are in a reference frame where the total momentum is zero, so that $\mathbf{p}_h=-(\mathbf{p}+\mathbf{p}')$, which explains why only the sum of the electronic momenta $\mathbf{p}+\mathbf{p}'$ appears. Finally, we may guess that the wave function, which is [17] just $t(\mathbf{p},\mathbf{p}')$ in the present case, is directly related to the excitonic ground-state wave function $1/(1+p_h^2)$. However, since we deal with the wave function for the two electrons, it is rather reasonable to guess that there is one such contribution for each electron so that

$$t(\mathbf{p},\mathbf{p}') = \left[\frac{1}{1+(\mathbf{p}+\mathbf{p}')^2}\right]^2. \quad (8)$$

One can insert these answers in Eq. (7), and one can perform analytically all the resulting integrations to check that they indeed satisfy Eq. (7). The check can also be easily performed numerically.

III. LIMITING CASES

Before going to our results for the generic situation, it is useful to consider the two limiting cases of very heavy and very light hole mass where the mass ratio $r=m_e/(m_e+m_h)$ goes either to 0 or 1. The Hamiltonian is

$$H = \frac{1}{2m_e}\left(\mathbf{p}_1^2+\mathbf{p}_2^2\right) + \frac{1}{2m_h}\mathbf{p}_3^2 + V(\mathbf{r}_1-\mathbf{r}_2) - V(\mathbf{r}_1-\mathbf{r}_3) - V(\mathbf{r}_2-\mathbf{r}_3), \quad (9)$$

where $V(\mathbf{r})=e^2/(4\pi\epsilon r)$ is the Coulomb interaction.

For $r\to 0$ (corresponding to $m_h \gg m_e$) we follow Bethe and Salpeter [23]. Going to the center-of-mass reference frame where $\mathbf{p}_3=-(\mathbf{p}_1+\mathbf{p}_2)$, the kinetic energy part H_c of the Hamiltonian becomes

$$H_c = \frac{1}{2\mu_{eh}}\left(\mathbf{p}_1^2+\mathbf{p}_2^2\right) + \frac{\mathbf{p}_1\cdot\mathbf{p}_2}{m_h}, \quad (10)$$

where $\mu_{eh}=m_e m_h/(m_e+m_h)$ is the exciton reduced mass. In the limit $r\to\infty$ only the first term is present. Hence, the effect of a finite m_h (in addition to the trivial modification of the exciton reduced mass) is to introduce the last term. This term gives the "mass-polarization correction," which turns out to be positive for the ground-state energy. This mass-polarization term was studied quite recently in detail by Filikhin *et al* [24]. For our purposes, for large m_h, the mass-polarization correction can be evaluated with the $m_h=\infty$ wave function, and the corresponding term in the energy is merely proportional to $1/m_h \propto r$ in this limit. Since it is positive, it gives to the trion binding energy a negative contribution, linear in r.

For the other limit $r\to 1$ (corresponding to $m_e \gg m_h$) it is more appropriate to take as new variables the position of the light mass, i.e., the hole, with respect to the center of mass of the two heavy ones $\boldsymbol{\rho}=\mathbf{r}_3-(\mathbf{r}_1+\mathbf{r}_2)/2$, together with half the distance between these two heavy masses $\mathbf{R}=(\mathbf{r}_2-\mathbf{r}_1)/2$. Taking again the center-of-mass reference frame, so that $\mathbf{p}_3=-(\mathbf{p}_1+\mathbf{p}_2)$, the conjugate momenta are $\pi_{\mathbf{R}}=\mathbf{p}_2-\mathbf{p}_1$ and $\pi_\rho=\mathbf{p}_3$, and the Hamiltonian is

$$H = \frac{1}{4m_e}\pi_{\mathbf{R}}^2 + \frac{1}{4}\left(\frac{1}{m_e}+\frac{2}{m_h}\right)\pi_\rho^2 + V(2\mathbf{R}) - V(\boldsymbol{\rho}+\mathbf{R}) - V(\boldsymbol{\rho}-\mathbf{R}). \quad (11)$$

In our limit this Hamiltonian can be handled by a Born-Oppenheimer treatment. In the case $m_e=\infty$, we have to deal with the problem of the hole in the presence of the attractive interaction by the two electrons, which are at fixed positions $\pm\mathbf{R}$. This corresponds to the Hamiltonian (11) without the electronic kinetic energy term $(1/4m_e)\pi_{\mathbf{R}}^2$. Let us call $E_\infty(\mathbf{R})$ the corresponding ground-state energy [including the repulsive $V(2\mathbf{R})$ contribution]. Let us call $\mathbf{R}_0$ the value of $\mathbf{R}$ for which its minimum is found. Considering now the case where m_e is quite large but not infinite, quantum fluctuations produce a departure of $\mathbf{R}$ from this minimum position $\mathbf{R}_0$. We set $\mathbf{R}=\mathbf{R}_0+\mathbf{u}$. For these fluctuations we can consider $E_\infty(\mathbf{R})$ an effective potential energy. Hence [25], we have to handle the Hamiltonian

$$H_{\mathrm{BO}} = \frac{1}{4m_e}\pi_{\mathbf{R}}^2 + E_\infty(\mathbf{R}). \quad (12)$$

For large m_e the fluctuations are small, so that we may expand $E_\infty(\mathbf{R})$ to lowest order around its minimum, $E_\infty(\mathbf{R}) = E_\infty(\mathbf{R}_0)+a\mathbf{u}^2$. In this way the Hamiltonian becomes

$$H_{\mathrm{BO}} = \frac{1}{4m_e}\pi_{\mathbf{u}}^2 + a\mathbf{u}^2 + E_\infty(\mathbf{R}_0). \quad (13)$$

This is the Hamiltonian of a three-dimensional harmonic oscillator, and accordingly, the ground-state energy is given by $E=E_\infty(\mathbf{R}_0)+(3/2)\hbar(a/m_e)^{1/2}$. In Eq. (13) we have assumed for the simplicity of the presentation that $E_\infty(\mathbf{R})$ is isotropic around its minimum. Clearly, this is not correct in general, and we should rather introduce the components $\mathbf{u}_\parallel$ and $\mathbf{u}_\perp$ of $\mathbf{u}$ parallel and perpendicular to $\mathbf{R}_0$, with corresponding coefficients $a_\parallel$ and $a_\perp$ for the expansion, so the parallel

TABLE I. Trion total binding energy $E_b(r)$ in atomic units as a function of the mass ratio of the electron to the exciton mass $r = m_e/(m_e + m_h)$. The exciton binding energy is 0.5.

r	Binding energy $E_b(r)$ (a.u.)
0	0.5282
0.05	0.5267
0.1	0.5256
0.15	0.5247
0.2	0.5240
0.25	0.5235
0.3	0.5233
0.35	0.5233
0.4	0.5235
0.45	0.5239
0.5	0.5246
0.55	0.5256
0.6	0.5270
0.65	0.5287
0.7	0.5310
0.75	0.5340
0.8	0.5378
0.85	0.5430
0.9	0.5503
0.95	0.5621
0.97	0.5696
0.98	0.5748
0.99	0.5821

and perpendicular harmonic oscillators do not have the same frequencies. But obviously, this does not change the final conclusion that $E - E_\infty(\mathbf{R}_0)$ is proportional to $m_e^{-1/2}$. Since in this large m_e situation $r = m_e/(m_e + m_h) \simeq 1 - m_h/m_e$ so that $m_e^{-1/2} \propto (1-r)^{1/2}$ and since the binding energy $E_b(r)$ is essentially the opposite of the energy, we come to the conclusion that, in the vicinity of $r = 1$, $E_b(r)$ behaves as $-(1-r)^{1/2}$.

IV. RESULTS

Our numerical results for $E_b(r)$ are given in Table I. Basically, we have made these calculations for $r = 0.05n$, with n going from 0 to 20. A finer mesh is unnecessary since the result for any r can be obtained from our results by an appropriate interpolation without significant loss of precision. This is what we have done in Fig. 1, where we have plotted $E_b(r)$ by making use of a spline interpolation. We have compared our results with those of Usukura *et al.* [22] for the mass ratios they have considered. They make use of the stochastic variational method with a correlated Gaussian basis. The agreement is quite fair, and it might very well be that the small differences are mostly due to the presentation of the results with respect to their precision. Details of the comparison are given in Table II.

By comparing our $r = 0$ result with much more precise variational calculations [26,27] which give a binding energy of $E_b(0) = 0.527751$ a.u., we see that we obtain a precision of 10^{-3}, which is somewhat less than the 10^{-4} we had in our preceding helium calculation but which is, nevertheless, quite enough for any practical goal. As we have indicated, this loss of precision is directly linked to the fact that the difference between the total trion energy and the exciton energy is small. As a result, when we subtract from our total trion energy the exciton binding energy of 0.5 a.u., we obtain 0.0282 a.u. for the binding energy of the second electron to the exciton, which is quite often called the trion binding energy. Our precision is then only about 2×10^{-2} because this binding is quite small. This is, nevertheless, sufficient for our purposes.

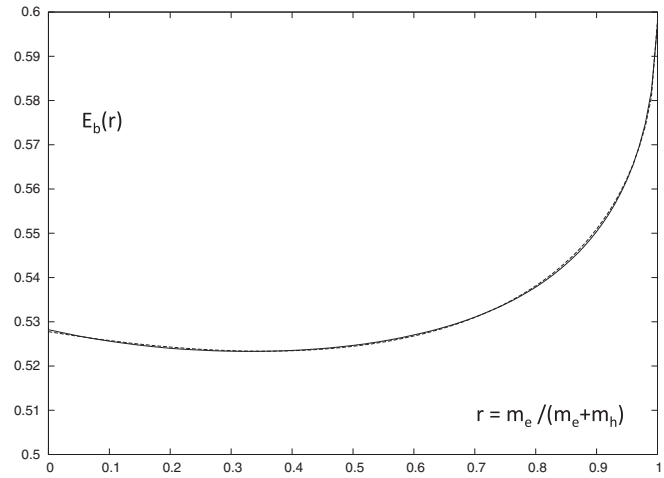

FIG. 1. Trion total binding energy $E_b(r)$ in atomic units as a function of the mass ratio of the electron to the exciton mass $r = m_e/(m_e + m_h)$. On this scale the exciton binding energy is 0.5. Solid line: spline interpolation through the results of Table I. Dashed line: fitting formula $E_b(r) = 0.71347 - 0.11527\, r - 0.18580\, \sqrt{1-r}$.

TABLE II. Comparison of our results with those of Usukura *et al.* [22] for the trion total binding energy. Usukura *et al.* use $\sigma = m_e/m_h$, from which our $r = \sigma/(1+\sigma)$ is obtained. Moreover, for $r > 0.5$, the roles of m_e and m_h in [22] are exchanged in comparison with our conventions. Our r and their σ are reported in the first two columns. Finally, they use as the energy unit the "excitonic Rydberg," so that finally, their binding energy $|E|$ is related to our $E_b(r)$ by $|E| = 2E_b(r)/(1+\sigma)$. We have chosen to convert our results $E_b(r)$ with this formula to compare them directly to [22]. The third column gives this converted (Conv.) $E_b(r)$, while the fourth column reports the results of [22] (specifically, the 3D results in their Table II, corresponding to the lines $-E$). Clearly, the agreement is quite good. Since after conversion our estimated precision is of the order of 10^{-3} (from comparison of our $r = 0$ result with [26,27]), we have stayed with this precision, which is also the one used by [22]. Note that, for $r = 1$, our result is the exact one (see text).

r	σ	Conv. $E_b(r)$	$\lvert E\rvert$ [22]
0	0	1.056	1.055
0.2857	0.4	0.747	0.746
0.4117	0.7	0.616	0.615
0.5	1	0.524	0.524
0.5882	0.7	0.619	0.619
0.7142	0.4	0.760	0.759
1	0	1.194	1.205

On the opposite side, for $r = 1$, our integral equation becomes singular as we have already mentioned, and accordingly, we have not done the corresponding numerical calculation. On the other hand, as can be seen in Table I, we have carried out calculations up to $r = 0.99$, which is quite close to $r = 1$. Our corresponding results have to be compared with variational calculations [28,29], giving $E_b(1) = 0.597139$ a.u. They turn out to be perfectly compatible with the analytical behavior $E_b(1) - E_b(r) \propto (1-r)^{1/2}$ we found in Sec. III. Hence, we have incorporated this value for $E_b(1)$ in our results to obtain Fig. 1, where the solid line is obtained from our results in Table I by a spline interpolation. One would expect a somewhat degraded precision in close vicinity to $r = 1$, which is singular to our calculations. However, we see no clear indication of such a loss at the level of our precision.

We believe that our precision is merely limited by our mesh in the modulus of wave vectors for $t(\mathbf{p}, \mathbf{p}')$: we have not been beyond 60 points because the computer time increases markedly when one goes to a finer mesh (40 points were quite enough in the helium case). One could think of more sophisticated ways to go around this problem, but there is no real point for such an effort since precision is not our primary purpose. On the other hand, with respect to the dependence on the angle between $\mathbf{p}$ and $\mathbf{p}'$, we have been near full convergence in this variable by going with Legendre polynomials up to $\ell = 20$, so we have been able to extrapolate in ℓ to improve our results. However, it is worth noting that the need to go to such high values of ℓ ($\ell = 5$ was enough in the helium case) seems to imply that the wave function is very structured, which clearly deserves further investigation. This is postponed to a future work.

Considering the dependence of the trion binding energy on the electron-hole mass ratio, one naturally has to keep in mind that the most important contribution comes trivially from the fact that our atomic energy unit is twice the exciton binding energy, which implies a result proportional to the exciton reduced mass $\mu_{eh} = m_e m_h/(m_e + m_h)$. Once this is taken into account, the trion binding energy is remarkably weakly dependent on the mass ratio since the binding energy stays approximately in the range [0.5233, 0.531] for r going from 0 to 0.7, which corresponds to a mass ratio m_e/m_h going to from 0 to 2.3. This comprises most of the practical range for standard semiconductors. This is in qualitative agreement with earlier findings [14].

To a large extent this weak dependence of the trion binding energy on the mass ratio is due to the fact that the trion is anyway weakly bound compared to the exciton binding energy itself. This is fairly clear on the $r = 0$ side since, compared to the free exciton, the additional electron is attracted by the fluctuating dipole of the exciton, which is a much weaker attractive potential than a bare charge. Hence, it is not surprising that the additional binding is roughly 6% of the exciton binding energy. On the $r = 1$ side the hole is attracted by the two infinitely heavy electrons, and there is no longer any quantum fluctuation in the attractive potential, so one may expect a stronger binding, which is, indeed, the case. However, the resulting binding is not much stronger, as is easily seen from the early perturbative calculations of Morse and Stueckelberg [30] for the equivalent hydrogen molecular ion problem, which gave a binding energy of 0.571 atomic units, not very far from the exact numerical result given above.

In addition to this narrow range of variation $E_b(r)$ presents a wide minimum. Indeed, as we saw in Sec. III, $E_b(r)$ decreases from its $r = 0$ value due to the mass-polarization correction. This correction happens to be fairly weak (it is zero if correlations between electrons in the ground-state wave function are neglected [23]), so $E_b(r)$ starts from $r = 0$ with a small negative slope. On the $r = 1$ side $E_b(r)$ starts from a somewhat higher value, but it drops more rapidly owing to the $E_b(1) - E_b(r) \propto (1-r)^{1/2}$ dependence we found in Sec. III. Hence, it reaches fairly rapidly values in the vicinity of the minimum. Inspection of Fig. 1 gives the feeling that the whole curve can be understood from these two limiting behaviors. In order to assert this statement more quantitatively we have tried to fit our results with an analytical expression, $E_b(r) = a - b\,r - c\,(1-r)^{1/2}$, involving only these behaviors. Amazingly, we have found that

$$E_b(r) = 0.71347 - 0.11527\,r - 0.18580\,\sqrt{1-r} \quad (14)$$

fits our numerical results perfectly within our estimated precision. This is plotted in Fig. 1 as the dashed line. Hence, we cannot exclude that this formula corresponds to an analytical result, although this seems extremely unlikely in view of the complexity of the problem. Note that it is natural to have a reasonable fit to the asymptotic behaviors on both sides, $r = 0$ and $r = 1$, but one would expect to need at least four independent constants. The surprising feature of Eq. (14) is that it contains only three constants and that, moreover, they provide a perfect fit over the whole range of r. Anyway, analytical or not, Eq. (14) has the advantage of showing that an understanding of $E_b(r)$ in the two limiting cases $r = 0$ and $r = 1$ allows an understanding of the whole $E_b(r)$. This might be a useful approach for the trion problem in situations other than the simple three-dimensional (3D) effective mass case that we have treated.

V. CONCLUSION

In this paper we have applied to the trion problem in semiconductors a general approach proposed previously for the three-body problem. This has been done in the simple case of a three-dimensional semiconductor with the effective mass approximation and bare Coulomb interaction. In this situation the trion is only weakly bound compared to the exciton. This brings practical complications to the numerical work, but beyond these details our procedure works without any problem. Our numerical results, which extend over the whole range of the electron-to-hole mass ratio, are in perfect agreement with existing earlier work making use of variational methods. In this paper we have not investigated the trion wave function, which comes out of the same numerical calculation as the trion binding energy. We expect this wave function to be fairly structured. We intend to proceed to this investigation in a future paper.

We have considered more specifically the cases of low or high electron-to-hole mass ratio. In these regimes the trion binding energy has a simple analytical dependence on the mass ratio. We have made use of these simple behaviors in these limiting cases to build an interpolation formula for

the whole domain of the electron-to-hole mass ratio. This formula contains only three parameters. Very surprisingly, it agrees perfectly well with our numerical results within our precision. Hence, it provides in practice the complete answer for the trion binding energy in the physical situation we have investigated. In more complicated situations this success points to the interest of investigating limiting cases in order to understand qualitatively, and perhaps quantitatively, the trion binding energy in the whole range of parameters of interest.

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