Ground State of Excitonic Molecules by the Green's-Function Monte Carlo Method

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The ground-state energy of excitonic molecules is evaluated as a function of the ratio of electron and hole masses, σ, with use of the Green's-function Monte Carlo method. For all σ, the Green's-function Monte Carlo energies are significantly lower than the variational estimates and in favorable agreement with experiments. In excitonic rydbergs, the binding energy of the positronium molecule ($\sigma = 1$) is predicted to be -0.06 and for $\sigma << 1$, the Green's-function Monte Carlo energies agree with the "exact" limiting behavior, $E = -2.346 + 0.764\sqrt{\sigma}$.

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Bound complexes of two electrons and two holes, known as biexcitons or excitonic molecules, have been observed in a variety of semiconductors.[1-5] In the effective-mass approximation with isotropic electron and hole masses, they are formally identical with hydrogen molecules except that the masses depend on the material and their ratio, $\sigma = m_e/m_h$, can vary between the limits of positronium ($\sigma = 1$) and hydrogen ($\sigma \ll 1$) molecules. Over the last thirty years, many theoretical attempts[6-10] have been made to investigate the variation of the ground-state energy of biexcitons with the electron-hole mass ratio σ. It has been shown rigorously that (i) the energy E should be symmetric around $\sigma = 1$ and vary monotonically in the range $0 < \sigma < 1$,[8] (ii) the slope $\partial E/\partial\sigma|_{\sigma=1} = 0$,[7] and (iii) in the limit $\sigma \to 0$, the energy should vary as $\sqrt{\sigma}$. The data for the hydrogen molecule can be represented by[7]

$$E = (-2.346 + 0.764\sqrt{\sigma})E_x, \qquad (1)$$

where $E_x = \mu e^4/2\hbar^2\kappa^2$ is the excitonic Rydberg, and μ and κ are the reduced mass, $m_e m_h/(m_e + m_h)$, and the dielectric constant, respectively.

In this Letter, the first Green's-function Monte Carlo (GFMC) calculation for the ground state of biexcitons is reported. It has been shown by Kalos and co-workers[11] that the GFMC method can be successfully applied to the calculation of exact ground-state energies of many-body boson systems. The possibility of extending such techniques to electronic structure problems has been investigated by Anderson,[12] Moskowitz *et al.*,[13] and Hirsch *et al.*[14] For biexcitons, the GFMC ground-state energies are considerably lower than the best variational estimates.[9] The GFMC binding energy of the positronium molecule ($-0.06\,E_x$) is a factor of 2 larger than the variational value, while close to the hydrogenic-molecule limit ($\sigma \ll 1$), the GFMC energies agree with Eq. (1) and hence with the experimental data.

The GFMC method derives from the formal similarity of the Schrödinger equation and a diffusion equation. This was first discussed by Metropolis[15] and subsequently developed by Kalos and co-workers.[11] The procedure outlined below is very similar to the one used by Moskowitz *et al.*[13] for LiH. The diffusion equation

$$-\tfrac{1}{2}\nabla_{\vec{R}}^2\psi_D(\vec{R},t) + A(\vec{R})\psi_D(\vec{R},t) = -\frac{\partial}{\partial t}\psi_D(\vec{R},t) \qquad (2)$$

and the Schrödinger equation are formally identical if the potential, $V(\vec{R})$, and the wave function, $\psi_S(\vec{R},-it)$, are identified with the absorption term, $A(\vec{R})$, and the probability function, $\psi_D(\vec{R},t)$, respectively. Here $\vec{R}$ denotes a vector with $3N$ components, N being the number of particles. If an arbitrary constant, E_r, is added to the Schrödinger equation and ψ_S is expressed in terms of a complete set of eigenfunctions, $\varphi_n(\vec{R})$, with eigenvalues, E_n, one finds

$$\begin{aligned}\psi_D(\vec{R},t) &= \psi_S(\vec{R},-it)\\ &= \sum_n a_n \varphi_n(\vec{R})\exp[-(E_n-E_r)t].\end{aligned}\tag{3}$$

For large times, only the lowest-order term will survive and $\psi_D = a_0\varphi_0(\vec{R})$, provided that E_r is chosen to be equal to E_0.

The time propagation of ψ_D is accomplished by the GFMC method. We write

$$\psi_D(\vec{R}_2,t_2) = \int d^{3N}R_1\, G(\vec{R}_2,t_2,\vec{R}_1,t_1)\psi_D(\vec{R}_1,t_1),\tag{4}$$

where G satisfies

$$\begin{aligned}&-\tfrac{1}{2}\nabla_{\vec{R}_2}{}^2 G(\vec{R}_2,t_2,\vec{R}_1,t_1)\\ &\quad+[V(\vec{R}_2)-E_r]\,G(\vec{R}_2,t_2,\vec{R}_1,t_1)\\ &\qquad= -\frac{\partial}{\partial t_2}G(\vec{R}_2,t_2,\vec{R}_1,t_1).\end{aligned}\tag{5}$$

Choosing a time step $\Delta t = |t_2 - t_1|$ small enough so that $U = V(\vec{R}_2) - E_r$ can be regarded as a constant, the solution of Eq. (5) can be written as

$$\begin{aligned}&G(\vec{R}_2,t_1+\Delta t,\vec{R}_1,t_1)\\ &\quad= (2\pi\Delta t)^{-3N/2}\exp\left[-\frac{(\vec{R}_2-\vec{R}_1)^2}{2\Delta t} - U\Delta t\right].\end{aligned}\tag{6}$$

Knowing G and some analytic trial function, $\psi_T(\vec{R}) = \psi_D(\vec{R},0)$, the asymptotic limit of $\psi_D(\vec{R},t)$ can be obtained by iterating Eq. (4) numerically through a stochastic simulation: A configuration $\vec{R}_1$ is propagated by first sampling $\vec{R}_2$ from the normalized Gaussian in Eq. (6) and then evaluating the weight $W(\vec{R}_2) = \exp(-U\Delta t)$. If $W(\vec{R}_2) < 1$, the configuration $\vec{R}_2$ is accepted with the probability W. However, if $W(\vec{R}_2) > 1$, the probability that a second configuration is created is $W(\vec{R}_2) - 1$ and with this probability a second identical configuration must also be accepted in $\psi_D(\vec{R}_2,t_2)$. The generalization to $W(\vec{R}_2) > 2$ is obvious. Iterative propagation eventually leads to the lowest eigenfunction φ_0.

There are two shortcomings in the above procedure: (i) The creation of configurations is a major source of statistical fluctuations, and (ii) the expression for G, Eq. (6), diverges when an electron approaches a hole. These can be remedied by the method of importance sampling.[11] Multiplying Eq. (4) with the trial function $\psi_T(\vec{R}_2)$ and defining $f(\vec{R},t) = \psi_T(\vec{R})\psi_D(\vec{R},t)$, one obtains

$$f(\vec{R}_2,t_2) = \int d^{3N}R_1\, K(\vec{R}_2,t_2,\vec{R}_1,t_1)f(\vec{R}_1,t_1),\tag{7}$$

where

$$K(\vec{R}_2,t_2,\vec{R}_1,t_1) = \psi_T(\vec{R}_2)G(\vec{R}_2,t_2,\vec{R}_1,t_1)/\psi_T(\vec{R}_1).\tag{8}$$

If $\psi_T(\vec{R})$ is close to $\varphi_0(\vec{R})$, the integral of K over $\vec{R}_2$ is close to unity which means that the absorption or creation of configurations rarely occurs and therefore $f(\vec{R},t)$ will be more stable than $\psi_D(\vec{R},t)$. Following Moskowitz *et al.*,[13] the short-time approximation is applied to Eq. (8). It should be noted that the short-time approximation of propagator K does not diverge.

The average energy of the system,

$$\langle E\rangle = \frac{\int d^{3N}R f(\vec{R},t)\{H\psi_T(\vec{R})/\psi_T(\vec{R})\}}{\int d^{3N}R f(\vec{R},t)},\tag{9}$$

is merely the average of $\psi_T{}^{-1}H\psi_T$ over the population of configurations obtained from the distribution $f(\vec{R},t)$. The difference between $\langle E\rangle$ and the exact ground-state energy arises because of finite time step Δt. In LiH, its effect on the total energy has been found to be 0.05%[16] and we expect it to be smaller for biexcitons. Effects of this size are negligible compared to the statistical uncertainty of our results.

In reduced units, the Hamiltonian of two electrons and two holes is

$$\begin{aligned}H = &-\frac{\mu}{m_e}(\nabla_1{}^2+\nabla_2{}^2) - \frac{\mu}{m_h}(\nabla_a{}^2+\nabla_b{}^2)\\ &+\frac{2}{r_{12}}+\frac{2}{r_{ab}}-\frac{2}{r_{1a}}-\frac{2}{r_{1b}}-\frac{2}{r_{2a}}-\frac{2}{r_{2b}}.\end{aligned}\tag{10}$$

For $m_e \neq m_h$, a generalization of the previous GFMC procedure is required. The trial function, $\psi_T(\vec{R})$, is taken to be a product of three functions, ψ_{ee}, ψ_{eh}, and ψ_{hh}, which are chosen such that the electrons and holes are treated on equal footing:

$$\begin{aligned}&\psi_{ee}(r) = \exp[c_1 r/(1+c_2 r)];\\ &\psi_{hh}(r) = \exp[c_3 r/(1+c_4 r)];\\ &\psi_{eh} = \exp[-(\alpha r_{1a}+\beta r_{1b}+\beta r_{2a}+\alpha r_{2b})]\\ &\qquad+\exp[-(\beta r_{1a}+\alpha r_{1b}+\alpha r_{2a}+\beta r_{2b})].\end{aligned}\tag{11}$$

The ground-state energy is independent of $\psi_T(\vec{R})$, although a better trial wave function reduces the variance in the calculation.

The GFMC calculations were performed for σ =0.01, 0.1, 0.3, 0.6, and 1.0. For each σ, the parameters c_1, c_2, c_3, c_4, α, and β were chosen by varying them individually to optimize the trial wave function. Then with a time step $\Delta t = 0.005$

in excitonic units (eu), $f(\vec{R},t)$ was propagated for 40 eu to allow convergence to the ground state. Energy averages and related variances were obtained over an additional time of several hundred eu.

Figure 1 shows the GFMC ground-state energies and the variational results of Brinkman, Rice, and Bell (BRB).[9] The former are significantly lower than the latter. For the positronium molecule, the GFMC binding energy, $-0.06E_x$, is twice as much as the variational value of BRB. For $\sigma = 0.01$, the GFMC ground-state energy, $(-2.268 \pm 0.004)E_x$, is in excellent agreement with the exact limiting behavior, $E = (-2.346 + 0.764\sqrt{\sigma})E_x$, but the GFMC binding energy, $0.268E_x$, is 20% larger than the value of BBR, $0.21E_x$. In CuBr and CuCl[1,2] where values of σ are estimated to be 0.01 and 0.02, the experimental measurements for the binding energy are $\simeq 29$ meV and between 34–44 meV, respectively. Taking E_x to be 110 and 190 meV (see Refs. 8 and 9), the GFMC binding energies in CuBr and CuCl are 29 and 45 meV, respectively. The GFMC slope, $\partial E/\partial\sigma$, is zero in the limit $\sigma \to 1$.

Recently, biexcitons have been observed in stressed Ge$\langle 1,1,16\rangle$[5] and Si$\langle 1,0,0\rangle$.[4] In Ge$\langle 1,1,16\rangle$ where electrons and holes occupy single, anisotropic conduction and valence bands, the binding energy has been estimated to be 0.15 ± 0.1 meV. Ignoring anisotropy, the GFMC value for the corresponding mass ratio $\sigma \simeq 0.7$ is -0.16 meV whereas the variational value[9] is -0.09 meV. Bednarek, Adamowskii, and Suffczynski[10] have shown that the anisotropy lowers the ground-state energies of both excitons and biexcitons, the former more so than the latter. As a result, the binding energy of biexcitons $(E - 2E_x)$ decreases with anisotropy and the GFMC value is therefore a lower bound on the experimental estimate. In $\langle 100\rangle$-stressed Si, Gourley and Wolfe[4] report the binding energy of biexcitons to be $-0.10E_x$ whereas in unstressed Si the experimental estimate[3] is $-0.08E_x$. For these two cases, the ratio of the optical masses is nearly unity and the corresponding GFMC value is $-0.06E_x$, compared to the variational value $-0.03E_x$.

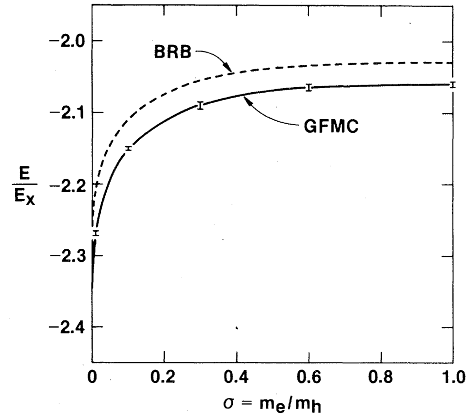

FIG. 1. Ground-state energy of biexcitons as a function of the electron-hole mass ratio, σ. The dotted curve represents the variational results of Brinkman, Rice, and Bell (BRB) (Ref. 9) while the solid curve shows the Green's-function Monte Carlo (GFMC) results. Here the energies are expressed in excitonic rydbergs, E_x.

In conclusion, the GFMC method leads to considerable improvement over the variational estimates for the ground-state energy of biexcitons. The overall effect is to bring the theoretical results into much better agreement with experimental measurements. The remaining discrepancies between these results and experiment are clearly due to band effects, and the current method should be extended to consider such questions. The GFMC technique should also be applied to multiexciton complexes for which considerable experimental data exist.[17] Recently, the ground-state properties of ^{4}He droplets have been investigated by this approach.[18] With appropriate modifications, similar calculations should be carried out for electron-hole droplets. Study of the energetics of the droplet as a function of size will yield its bulk, surface, and curvature energies which can be used to test the accuracy of the existing many-body and density functional calculations.[17]

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