Efficient numerical method for calculating exciton states in quantum boxes

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Abstract

We have developed an efficient numerical method for exciton states confined in quantum boxes. The exciton wave function is expanded in terms of discrete variable representation basis functions. Our numerical approach has proved to be computationally much less demanding in comparison with the conventional configuration-interaction one.

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1. Introduction

Semiconductor nanostructures based on advanced fabrication technologies [1–3] have attracted considerable attentions in recent years due to their wide range applications to functional materials [4–6]. In the nanostructures, the quantum confinement has a great influence on excitonic properties, such as density of states, binding energy, and oscillator strength. These properties are highly relevant to the functions inherent in the semiconductor nanostructures. Since the confinement effects strongly depend on dimensions, sizes, and shapes of the nanostructures, it is crucial to elucidate the exciton states in various nanostructures.

Exciton states confined in nanostructures have often been investigated theoretically by using either a variational approach [7,8] or a configuration-interaction (CI) approach [7,9]. In the variational approach, the exciton wave function is represented by a trial function. Validity of the approach depends on the choice of the trial function and, in general, its application to excited exciton states is practically difficult. In the conventional CI (cCI) approach, on the other hand, the wave function is ex-

panded in terms of an appropriate basis set, and thus the ground and excited states can be described accurately with a large number of bases. As will be shown later, the cCI approach requires huge computational costs due to the multi-dimensional integrals to calculate the Coulomb matrix elements. As a result, the cCI approach is not suitable for calculating multi-exciton states, dynamics of excitons, or excitons in complex nanostructures.

In the present study, we have developed an efficient numerical method for calculating exciton states confined in nanostructures. To overcome the drawback of the cCI approach mentioned above, we adopt the discrete variable representation (DVR) for constructing a basis set [11–14]. The DVR method has been employed intensively in molecular science and proved to be a powerful and efficient manner to calculate molecular properties [15,16]. In the DVR-based CI (DVR-CI) approach, the Coulomb matrix is reduced to a diagonal matrix having single-point values with no integrals. This desirable property is due to the fact that the DVR basis functions are coordinate eigenfunctions localized on each grid point associated with the Gaussian quadrature rule and satisfy the Kronecker delta property at the grid points. To confirm the numerical advantage of the DVR-CI approach over the cCI one, we fully compare the results obtained by the two approaches.

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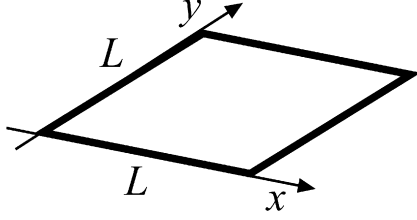 *E-mail address:* nobusada@ims.ac.jp (K. Nobusada).

Fig. 1. Schematic diagram of a two-dimensional quantum box with width L.

2. Method of calculation

We consider exciton states confined in nanostructures. The Hamiltonian operator is given by

$$\mathcal{H} = \sum_{i=e,h} \left[-\frac{\hbar^2}{2m_i}\nabla_i^2 + V_i(\vec{r}_i) \right] - \frac{e^2}{\epsilon r_{e-h}}, \tag{1}$$

where m_e and m_h are the electron and hole effective masses. The last term in Eq. (1) is the electron–hole Coulomb interaction potential with e and ϵ being the elementary charge and the dielectric constant, respectively. V_e (V_h) is the confinement potential for the electron (hole), which is determined by the confined structure. Although the present method is generally applicable to various types of nanostructures, we choose a two-dimensional square box with width L as an example (see Fig. 1). The confinement potential is given in the form of

$$V_i(\vec{r}_i) = \begin{cases} 0 & \text{for } 0 < x_i < L \text{ and } 0 < y_i < L, \\ \infty & \text{otherwise,} \end{cases} \tag{2}$$

where $\vec{r}_i = (x_i, y_i)$.

In the cCI approach, the exciton wave function can be expanded in terms of products of the electron and hole single-particle eigenfunctions [7,9]

$$\phi_{jlmn} = \frac{2}{L}\sin(k_j x_e)\sin(k_l y_e)\frac{2}{L}\sin(k_m x_h)\sin(k_n y_h),$$
$$j, l = 1, \ldots, N_e, \ m, n = 1, \ldots, N_h, \tag{3}$$

where $k_j \ (= \pi j/L)$ refers to the wave number, and N_e and N_h are the number of basis functions for the electron and hole states, respectively. Then, the Hamiltonian matrix is written by

$$H_{\substack{jlmn \\ j'l'm'n'}} = E_{jlmn}^{(0)}\delta_{jj'}\delta_{ll'}\delta_{mm'}\delta_{nn'}$$
$$+ \int d\vec{r}_e \int d\vec{r}_h \phi_{jlmn}\frac{-e^2}{\epsilon r_{e-h}}\phi_{j'l'm'n'}, \tag{4}$$

$$E_{jlmn}^{(0)} = \frac{\hbar^2}{2m_e}(k_j^2 + k_l^2) + \frac{\hbar^2}{2m_h}(k_m^2 + k_n^2). \tag{5}$$

This expression clearly shows that the computation of the matrix H requires the order of N^2 four-dimensional numerical integrals, where $N \ (= N_e^2 N_h^2)$ is the dimension of the matrix H. In the case of a three-dimensional square box, N^3 six-dimensional numerical integrals are required. These multi-dimensional integrals are apparently computationally demanding and become a practical difficulty in calculating exciton states [9,10].

To reduce the computational costs of the cCI approach, we alternatively use DVR to construct the basis set. In the DVR-CI

formalism, the single-particle basis functions are transformed into the grid-point ones. The transformation matrix is determined by the grid points and the weights associated with an appropriate Gaussian quadrature rule [11]. Since the second term in Eq. (4) can be evaluated by the Gauss–Chebyshev quadrature of the second kind [17], we use the Gauss–Chebyshev DVR [18]. The grid points are given by

$$x_{e,s} = \frac{L}{N_e + 1}s, \quad s = 1, \ldots, N_e, \tag{6}$$

and the weights are constants, $w_{xe,s} = L/(N_e + 1)$. For the other coordinates y_e, x_h, and y_h, the grid points and the weights are given in a similar way. Then, the transformation matrix is derived in the form of

$$U_{\substack{stuv \\ jlmn}} = \sqrt{w_{xe,s}w_{ye,t}w_{xh,u}w_{yh,v}}\,\phi_{jlmn}(\vec{r}_{e,st}, \vec{r}_{h,uv})$$
$$= \frac{2}{N_e + 1}\sin(k_j x_{e,s})\sin(k_l y_{e,t})$$
$$\times \frac{2}{N_h + 1}\sin(k_m x_{h,u})\sin(k_n y_{h,v}). \tag{7}$$

We finally obtain the matrix H in DVR as follows:

$$H_{\substack{stuv \\ s't'u'v'}}^{(\text{DVR})} = \left[UHU^{-1} \right]_{\substack{stuv \\ s't'u'v'}}$$
$$= T_{ss'}^{(e)}\delta_{tt'}\delta_{uu'}\delta_{vv'} + T_{tt'}^{(e)}\delta_{ss'}\delta_{uu'}\delta_{vv'}$$
$$+ T_{uu'}^{(h)}\delta_{ss'}\delta_{tt'}\delta_{vv'} + T_{vv'}^{(h)}\delta_{ss'}\delta_{tt'}\delta_{uu'}$$
$$- \frac{e^2}{\epsilon|\vec{r}_{e,st} - \vec{r}_{h,uv}|}\delta_{ss'}\delta_{tt'}\delta_{uu'}\delta_{vv'}, \tag{8}$$

where T denotes the kinetic energy term given by [19]

$$T_{ss'}^{(i)} = \frac{\hbar^2}{2m_i}\frac{\pi^2}{L^2}\frac{(-1)^{s-s'}}{2}\left\{ \left[\sin^2\frac{\pi}{2(N_i+1)}(s-s') \right]^{-1} \right.$$
$$\left. - \left[\sin^2\frac{\pi}{2(N_i+1)}(s+s') \right]^{-1} \right\} \quad \text{for } s \neq s',$$
$$= \frac{\hbar^2}{2m_i}\frac{\pi^2}{L^2}\frac{1}{2}\left\{ \frac{1}{3}\left[2(N_i+1)^2 + 1 \right] \right.$$
$$\left. - \left[\sin^2\frac{\pi}{N_i+1}s \right]^{-1} \right\} \quad \text{for } s = s'. \tag{9}$$

Owing to the great advantage of DVR, the matrix of the multi-dimensional Coulomb integrals [Eq. (4)] is reduced to the diagonal matrix with single-point values [12]. Consequently, the computational time for the matrix elements decreases sharply. In addition, the matrix H becomes very sparse, i.e., the number of nonzero elements is only $N \times (2N_e + 2N_h)$. Therefore, we can deal with a large size of Hamiltonian matrix by combining the Lanczos diagonalization. These great advantages allow us to calculate even the excited exciton states very efficiently. The eigenvalues of H correspond to the energy of each exciton state E^{ex}, and the exciton wave function is expressed by

$$\Psi(\vec{r}_e, \vec{r}_h) = \sum_{stuv} a_{stuv}\phi_{stuv}^{(\text{DVR})}(\vec{r}_e, \vec{r}_h)$$
$$= \sum_{\substack{stuv \\ jlmn}} a_{stuv}U_{\substack{stuv \\ jlmn}}\phi_{jlmn}(\vec{r}_e, \vec{r}_h), \tag{10}$$