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2008 J. Phys.: Condens. Matter 20 055211

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An optimized configuration interaction method for calculating electronic excitations in nanostructures

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Received 25 July 2007, in final form 29 November 2007

Published 17 January 2008

Online at stacks.iop.org/JPhysCM/20/055211

Abstract

The configuration interaction method has been widely used to calculate electronic excitations in nanostructures, but it suffers from a slow rate of convergence with the number of configurations in the basis set and from the inability to select *a priori* the most important configurations. The optimized configuration interaction method presented here removes the limitations of the conventional approach by identifying at the outset the configurations that are most relevant for describing electronic excitations. We show that the ‘best’ configurations are remarkably different from the configurations that one would expect on the basis of the single-particle energy ladder, and that a small, optimized set of configurations predicts excitation energies with accuracy comparable to that for much larger, non-optimized sets of configurations. This approach opens the way to a new generation of configuration interaction methods where the configurations are pre-selected using heuristic search methods.

The configuration interaction (CI) method [1] dates back to the origins of quantum mechanics, and for many decades it has been the primary tool to calculate the electronic states of atoms and molecules. In this approach, the many-body electronic wavefunctions are expanded in a set of Slater determinants (configurations) constructed by selecting a reference configuration and promoting one or more electrons from occupied to unoccupied single-particle states. The development of new iterative diagonalization algorithms and powerful computational capabilities has made possible CI calculations including millions of configurations. These large-scale CI calculations provide benchmarks against which less rigorous theories of electronic structure are being tested.

In the last decade, the CI method has been extensively applied to calculate electronic excitations in semiconductor nanostructures [2–11]. These studies include calculations of excitonic energies and optical absorption spectra in quantum dots [2, 3], excitonic fine structure [4, 5], carrier relaxation times [6], multi-exciton recombination rates [7, 8], electron and hole charging spectra [9, 10], and quantum entanglement in quantum dot molecules [11]. The standard approach to CI calculations for semiconductor nanostructures [2–11] consists of selecting an active space of occupied and unoccupied single-particle states, and generating all the configurations consistent with that space. This approach, however, suffers

from serious drawbacks, that limit its accuracy and range of applicability: (i) The CI expansion converges slowly with the dimension of the active space, or, equivalently, with the number of configurations. This is illustrated in figure 1(a), which shows the convergence of the bi-exciton ground-state energy of a 39 Å diameter CdSe quantum dot (calculated using the semi-empirical pseudopotential method described below) as a function of the total number of configurations. While the effects of configuration mixing are relatively small (<100 meV) on an absolute energy scale, the slow convergence of the CI expansion may significantly impact the accuracy of calculated energy differences, such as the bi-exciton binding energy [12]. (ii) This problem is compounded by the difficulty of identifying *a priori* the configurations that give the largest contribution to the CI expansion. Figure 1(b) shows the ex-post-facto decomposition of the bi-exciton ground state (calculated using 119 340 configurations), as a function of the single-particle energy of the configurations included in the CI basis set³. We see that a few configurations that are 300 meV or more above the lowest-energy configuration have a non-negligible contribution to the ground-state wavefunction, while a large number of configurations that are lower in energy do not contribute to the ground-state wavefunction. Thus, truncating

³ In this work, the term ‘basis set’ is used to indicate the set of configurations used to expand the many-particle wavefunctions.

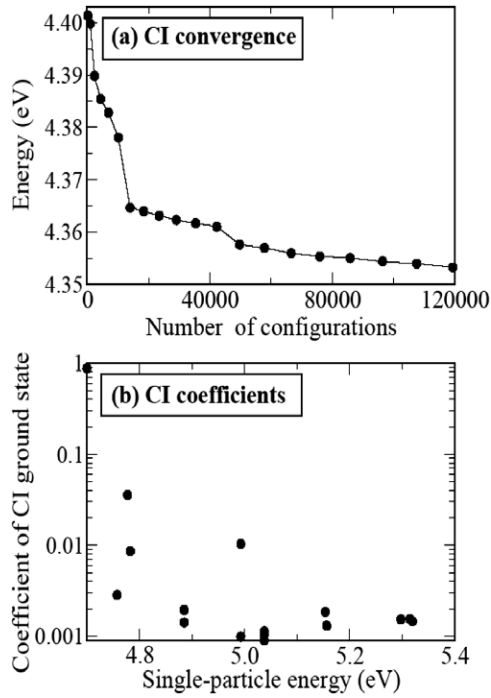


Figure 1. (a) Ground-state bi-exciton energy of a 39 Å diameter CdSe quantum dot as a function of the total number of configurations included in the basis set. The configurations are selected by fixing the number of conduction states ($n_C = 9$) and varying the number of valence states ($n_V = 1-20$). (b) Decomposition of the bi-exciton ground state as a function of the single-particle energy of the configurations in the CI basis set.

the CI expansion according to the single-particle energy of the configurations may be wasteful, as the computational effort scales at least quadratically with the number of configurations. What is needed is the capability to select at the outset the most important configurations.

A few approaches have been proposed in the quantum-chemistry literature to select relevant configurations for CI calculations of small molecules. Feller [13] proposed an iterative approach where a set of reference configurations is selected and sequentially augmented by adding single- and double-substitution configurations that, upon diagonalization of the CI matrix, are found to give a large contribution to the CI ground state. Mitrushenkov [14] proposed a ‘dynamical CI’ method where, at each step of the iterative diagonalization procedure, only configurations that have weight larger than a pre-assigned value are retained. Similarly, Greer [15] suggested an iterative approach where randomly selected configurations are added to the basis set, and unimportant configurations are removed from the basis set. To the best of our knowledge, none of these approaches has ever been applied to semiconductor nanostructures, and it is likely that such methods would be computationally very expensive for nanostructure calculations.

In this work, we propose a method to select *a priori* the most relevant configurations that describe electronic excited states in nanostructures. For a given active space and a given number of configurations N , we identify via heuristic search methods the ‘best’ set of configurations, i.e. the N

configurations that minimize the energy of the electron system. We demonstrate this method in the case of single excitons and bi-excitons in CdSe quantum dots, and show that the optimized configurations are different from those that one would expect based on the single-particle energy ladder. We also show that a small basis set of optimized configurations yields excitation energies with accuracy comparable to much larger non-optimized configuration basis sets. The practical importance of the present approach is twofold: (i) it allows one to pre-select the configurations that are most relevant to describe electronic excitations, and (ii) when coupled with a robust search algorithm, it provides a computationally more efficient alternative to standard CI calculations.

The CI method has been used in combination with several different approaches to solve the underlying single-particle Schrödinger equation: Single-band effective mass [16, 17] multi-band effective mass [18], effective bond orbital models [19], tight binding [4, 20] and semi-empirical pseudopotentials [21]. Here we choose the plane-wave empirical pseudopotential method, which has been successfully used in the past to study electronic excitations in colloidal nanocrystal [21, 22]. The single-particle Schrödinger equation has the form:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) + \hat{V}_{\text{NL}} + \hat{V}_{\text{SO}} \right] \psi_i(\mathbf{r}, \sigma) = \varepsilon_i \psi_i(\mathbf{r}, \sigma), \quad (1)$$

where $V(\mathbf{r}) = \sum_{\mathbf{R}} v(\mathbf{r} - \mathbf{R})$ is a local pseudopotential (given by the superposition of screened atomic potentials), \hat{V}_{NL} is a non-local pseudopotential operator, and \hat{V}_{SO} is the spin-orbit potential operator. The screened atomic potentials, as well as \hat{V}_{NL} and \hat{V}_{SO} , are fitted to measured bulk transition energies, effective masses, and deformation potentials, and to *ab initio* calculated bulk wavefunctions [23]. Equation (1) is solved by expanding the wavefunctions in a plane-wave basis set, and using the folded-spectrum method [24] to obtain the band-edge single-particle energies and wavefunctions. In the next step, we construct the many-particle CI Hamiltonian:

$$\begin{aligned} \hat{H}_{\text{CI}} = & \sum_{i \in C} \varepsilon_i c_i^* c_i - \sum_{j \in V} \varepsilon_j d_j^* d_j + \frac{1}{2} \sum_{ijkl \in C} J_{ijkl}^{CC} c_i^* c_j^* c_l c_k \\ & + \frac{1}{2} \sum_{ijkl \in V} J_{ijkl}^{VV} d_i^* d_j^* d_l d_k \\ & - \sum_{ik \in V, jl \in C} (J_{ijkl}^{VC} - K_{ijkl}^{VC}) c_i^* d_j^* c_l d_k. \end{aligned} \quad (2)$$

Here $c_i^*(c_i)$ is the creation (annihilation) operator for an electron in the conduction-band state i , $d_i^*(d_i)$ is the creation (annihilation) operator for a hole in the valence-band state i , and $V(C)$ denote the valence-band (conduction-band) manifolds included in the active space. To reduce the complexity of the problem, we diagonalize the CI Hamiltonian separately in the subspace of single excitations (mono-excitons), double excitations (bi-excitons), etc. The Coulomb and exchange integrals of equation (2) are screened by the dielectric constant $\varepsilon(\mathbf{r}, \mathbf{r}')$ of the nanostructure, as discussed in [21]:

$$\begin{aligned} J_{ijkl} = & \sum_{\sigma\sigma'} \int \psi_i^*(\mathbf{r}, \sigma) \psi_j^*(\mathbf{r}', \sigma') \frac{e^2}{\varepsilon(\mathbf{r}, \mathbf{r}') |\mathbf{r} - \mathbf{r}'|} \\ & \times \psi_k(\mathbf{r}, \sigma) \psi_l(\mathbf{r}', \sigma') d\mathbf{r} d\mathbf{r}'. \end{aligned} \quad (3)$$

Table 1. Single-particle energies of the first few electron and hole states included in the active space. The letters in parenthesis denote the dominant angular-momentum character of the corresponding envelope functions. The energy zero is the top of the valence-band (state h_1).

Hole states	Energy (eV)
h_1 (s)	0.000
h_2 (s)	-0.029
h_3 (p)	-0.039
h_4 (p)	-0.041
h_5 (p + d)	-0.139
h_6 (p + d)	-0.146
h_7 (p + d)	-0.146
Electron states	Energy (eV)
e_1 (s)	2.350
e_2 (p)	2.649
e_3 (p)	2.657
e_4 (p)	2.660

We describe next the optimized configuration interaction (OCI) algorithm, which includes three steps:

- (i) We start by selecting an active space consisting of the n_V highest-energy single-particle occupied levels and the n_C lowest-energy single-particle unoccupied levels.
- (ii) Next, we choose the number of orbital configurations (N_{OC}), which will be subjected to the optimization procedure. Each orbital configuration is defined by the occupation numbers $\{p_i, q_j\}$ of the single-particle energy levels belonging to the active space. Here p_i is the number of holes in the valence-band level i and q_j is the number of electrons in the conduction-band state j . Since each single-particle level is spin degenerate, $p_i, q_j = 0, 1, 2$. Furthermore, since we are considering only specific excitation levels, the number of electrons and holes m is fixed: $\sum_{i=1}^{n_V} p_i = \sum_{j=1}^{n_C} q_j = m$. The maximum number of orbital configurations compatible with a given active space is $M_{OC} = n_V n_C$ for a single-exciton ($m = 1$) and $M_{OC} = n_V n_C (n_V + 1)(n_C + 1)/4$ for a bi-exciton ($m = 2$).
- (iii) The set of N_{OC} optimized configurations is then determined using a Monte-Carlo simulated-annealing search algorithm [25]. Starting from an initial set of randomly selected orbital configurations, $\{\sigma_1, \sigma_2, \dots, \sigma_{N_{OC}}\}$, we construct the set of Slater determinants that includes all the spin configurations consistent with the selected orbital configurations. The CI Hamiltonian of equation (2) is diagonalized in this basis set using an iterative diagonalization algorithm to find the lowest-energy eigenstates. Next, we randomly select one of the N_{OC} orbital configurations, e.g. σ_i , and promote one electron (or one hole) to a different energy level. This operation replaces the configuration σ_i with a new configuration σ_i^{new} , while keeping the total number of orbital configurations N_{OC} fixed. We then construct the set of Slater determinants corresponding to the new set of orbital configurations, and diagonalize the CI Hamiltonian in this new basis set. This move is accepted with probability $P = e^{-\Delta E/K_B T}$, where

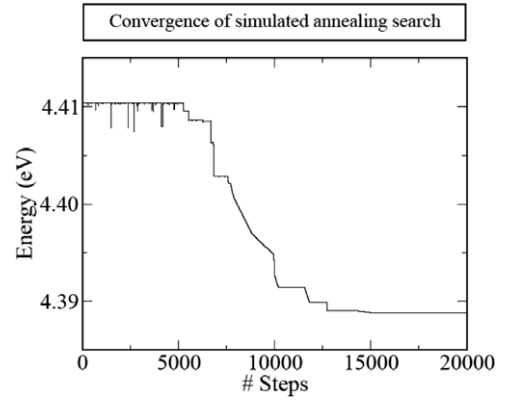


Figure 2. Convergence rate of the simulated-annealing algorithm shown for a bi-exciton with $N_{OC} = 4$.

$\Delta E = E_{GS}^{\text{new}} - E_{GS}^{\text{old}}$ is the difference between the ground-state energies of the new and old sets of configurations, k_B is the Boltzmann constant, and T is the simulated-annealing temperature. If the move is accepted, we repeat step (iii) starting from the new set of configurations $\{\sigma_1, \sigma_2, \dots, \sigma_i^{\text{new}}, \dots, \sigma_{N_{OC}}\}$; otherwise, a different configuration σ_j is randomly selected and replaced by a new configuration σ_j^{new} , until the move is accepted. The initial value of the simulated-annealing temperature T is chosen so that approximately 50% of the moves are accepted. The temperature T is then slowly decreased until the global energy minimum, corresponding to the ‘best’ set of N_{OC} orbital configurations, is found [25].

To illustrate the optimization algorithm, we consider a CdSe quantum dot having a diameter of 39 Å. The quantum dot is constructed by cutting out a spherical segment of bulk CdSe in the wurtzite lattice structure. The surface Cd and Se atoms are passivated by ligand potentials [22]. The screened atomic potentials used in equation (1) are taken from [23]. The Coulomb and exchange integrals (equation (3)) are screened by a distance-dependent and size-dependent dielectric function [21]. Table 1 summarizes the band-edge single-particle states of the quantum dot. The first electron state (e_1) has an s-like envelope function, while the next three electron states (e_2, e_3, e_4) have p-like envelope functions.

The convergence rate of the simulated-annealing algorithm is shown in figure 2 in the case of $m = 2$ (bi-exciton) and $N_{OC} = 4$. The active space consists of $n_V = 20$ valence-band levels and $n_C = 9$ conduction-band levels, for a total of $M_{OC} = 9450$ bi-exciton configurations. The number of possible choices for the four orbital configurations in the OCI basis set (i.e. the dimension of the OCI search space) is 3.32×10^{14} . The initial annealing temperature is set to $T_0 = 0.1$ eV. The temperature is decreased every 50 steps by a factor of 0.94, i.e. $T_{n+1} = 0.94 T_n$. We see from figure 2 that fewer than 15 000 simulated-annealing steps are sufficient to identify the best set of orbital configurations. Similar convergence profiles are obtained starting from different sets of initial configurations. We find that, out of 20 initial sets of randomly selected orbital configurations, the simulated-annealing algorithm converges to the same set of optimized configurations 100% of the times.

Table 2. Optimized and non-optimized (Aufbau) sets of orbital configurations for the single-exciton (X) and bi-exciton (XX) ground state. The configurations are described by the single-particle levels occupied by the holes and the electrons. The numbers in parenthesis are the amplitudes (in %) of the coefficients of the CI expansion.

	N_{OC}	Optimized	Aufbau
X	4	h_1, e_1 (98.5)	h_1, e_1 (~ 100)
		h_3, e_2 (0.5)	h_2, e_1 (< 0.1)
		h_4, e_4 (0.3)	h_3, e_1 (< 0.1)
		h_7, e_3 (0.7)	h_4, e_1 (< 0.1)
	5	h_1, e_1 (98.3)	h_1, e_1 (99.9)
		h_3, e_2 (0.5)	h_2, e_1 (< 0.1)
		h_4, e_4 (0.3)	h_3, e_1 (< 0.1)
		h_{13}, e_4 (0.7)	h_4, e_1 (< 0.1)
		h_7, e_3 (0.2)	h_5, e_1 (0.1)
	XX	4	$h_1 h_1, e_1 e_1$ (91.7)
$h_3 h_3, e_1 e_1$ (5.5)			$h_1 h_2, e_1 e_1$ (< 0.1)
$h_7 h_7, e_1 e_1$ (1.9)			$h_1 h_3, e_1 e_1$ (< 0.1)
$h_1 h_7, e_1 e_3$ (0.9)			$h_1 h_4, e_1 e_1$ (0.9)
5		$h_1 h_1, e_1 e_1$ (91.8)	$h_1 h_1, e_1 e_1$ (97.0)
		$h_3 h_3, e_1 e_1$ (5.2)	$h_1 h_2, e_1 e_1$ (< 0.1)
		$h_7 h_7, e_1 e_1$ (1.6)	$h_1 h_3, e_1 e_1$ (< 0.1)
		$h_1 h_7, e_1 e_3$ (0.6)	$h_1 h_4, e_1 e_1$ (0.7)
		$h_1 h_7, e_1 e_4$ (0.8)	$h_2 h_2, e_1 e_1$ (2.3)

The optimized sets of single-exciton and bi-exciton configurations obtained from the simulated-annealing search are shown in table 2 in the cases $N_{OC} = 4$ and $N_{OC} = 5$. For comparison, the non-optimized sets of ‘Aufbau’ configurations that minimize the *single-particle* energy are also shown in table 2. We find that (i) the configurations in the optimized set are different from those in the non-optimized set (see table 2), and are largely unexpected. For example, the inclusion of configurations where one of the electrons (or one of the holes) is in a p-like state (e.g. e_2-e_4) tends to lower the CI energy significantly, although the single-particle energy of such configurations is quite large, as can be gleaned from table 1. We also find (ii) that the set of N_{OC} optimized configurations is in general different from the set of N_{OC} orbital configurations that contribute the most to the full-CI (FCI) ground-state wavefunction. For example, in the case of the bi-exciton ground state, the set of 4 optimized configurations includes the configuration ($h_1 h_7, e_1 e_3$) (see table 2), while the set of 4 configurations that contribute the most to the FCI ground state includes the configuration ($h_4 h_4, e_1 e_1$). This result implies that the set of optimized configurations cannot be always derived *a posteriori* from the knowledge of the CI ground state. Finally, we find that (iii) the set of N_{OC} optimized configurations is a subset of the $N_{OC} + 1$ optimized configurations (compare $N_{OC} = 4$ and $N_{OC} = 5$ in table 2), and that the additional configuration in the $N_{OC} + 1$ set often has larger weight than some of the configurations in the N_{OC} set.

We now discuss the efficiency of the OCI method compared with the conventional CI method. Note that the OCI expansion is exact (i.e. the OCI energy coincides with the FCI energy) when all the configurations in the active space are included. Figure 3 shows the single-exciton and bi-exciton ground-state correlation energy as a function of the

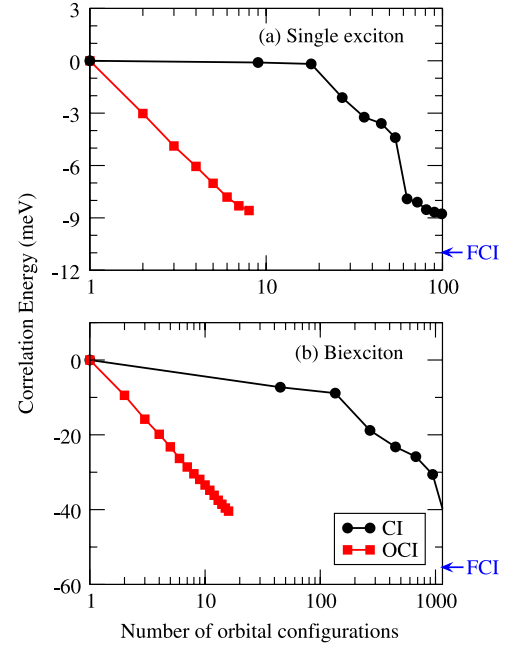


Figure 3. Correlation energy of the (a) single-exciton and (b) bi-exciton ground states as a function of the number of orbital configurations. Red squares show the results of the optimized CI approach, while black circles show the results of the conventional CI approach, where the CI configurations were selected by fixing the number of conduction states ($n_c = 9$) and varying the number of valence states ($n_v = 1-20$). The FCI correlation energy (obtained by including all the configurations in the active space) is shown by a horizontal arrow.

(This figure is in colour only in the electronic version)

number of orbital configurations N_{OC} included in the CI basis set. The correlation energy is defined here as $E_{GS}(N_{OC}) - E_{GS}(1)$. We find that the OCI method converges much faster with the number of configurations than the conventional CI method. For example, five optimized orbital configurations ($N_{OC} = 5$) give the bi-exciton ground-state energy with accuracy comparable to ~ 450 non-optimized configurations. Similarly, ten optimized configurations ($N_{OC} = 10$) are equivalent to ~ 1000 non-optimized configurations. Thus, the OCI approach requires about two orders of magnitude fewer configurations than the conventional CI approach to achieve similar accuracy. If iterative diagonalization methods are used to find the lowest-energy eigenstates of the CI Hamiltonian, the computational cost scales with the number of configurations as N_{OC}^2 . As a result, the OCI method would be four orders of magnitude more efficient than the conventional CI method, if the set of optimized configurations was known in advance. The simulated-annealing search algorithm requires ~ 10000 steps to find the set of optimized configurations (figure 2), thus making the computational cost of the OCI method comparable to that of the conventional CI approach.

However, the efficiency of the search method can be dramatically increased by taking advantage of the above-mentioned property that the set of $N_{OC} + 1$ optimized configurations includes the set of N_{OC} optimized configurations (see table 2). This property suggests the following recursive search

algorithm: if the set of n optimized configurations is known, the set of $n + 1$ optimized configuration can be determined by searching the space of orbital configurations for the additional configuration that minimizes the energy of the $n + 1$ set. This search can be performed using the simulated-annealing algorithm or other heuristic algorithms.

The advantage of the recursive search method is that the dimension of the search space is only $\sim M_{OC}$ (the total number of orbital configurations in the active space), which is orders of magnitude smaller than the dimension of the simulated-annealing search space $\binom{M_{OC}}{N_{OC}}$. The smaller dimension of the search space more than compensates for the need to search the configuration space at each step $n = 1, \dots, N_{OC}$ of the recursive algorithm. As a result, the recursive search method is significantly faster than either the simulated-annealing OCI approach or the conventional CI diagonalization approach. For example, in the case of the bi-exciton ground state, we found that the recursive search algorithm is almost one order of magnitude faster than the simulated-annealing OCI or the conventional CI algorithm.

The OCI method can be generalized to find higher-energy excited states by minimizing the sum of the energies of the first several CI states. For example, if the m lowest-energy bi-exciton states are sought, one can determine the optimized set of configurations that minimize the energy $E = \sum_{i=1}^m E_i$, where E_i is the energy of the i th lowest bi-exciton state. In this case, the computational cost of the OCI method scales linearly with m .

In conclusion, we have presented a theoretical approach to the selection of the ‘best’ configurations for configuration interaction calculations of electronic excitations in nanostructures. We find that the set of optimized configurations is different from what one would expect based on the single-particle energy ladder. Our method makes it possible to identify *a priori* the configurations that are relevant to describe electronic excitations in nanostructures. When coupled with an efficient search algorithm, it also provides a more efficient computational approach compared to standard CI calculations.

Acknowledgments

This work was funded by the US Department of Energy, Office of Science, Basic Energy Sciences, under Contract

No. DE-AC36-99GO10337 to NREL. This research used resources of the National Energy Research Scientific Computing Center, which is supported by the Office of Science of the US Department of Energy under Contract No. DE-AC03-76SF00098.

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