Linear scaling approach for atomistic calculation of excitonic properties of 10-million-atom nanostructures

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Numerical calculations of excitonic properties of novel nanostructures, such as nanowire and crystal phase quantum dots, must combine atomistic accuracy with an approachable computational complexity. The key difficulty comes from the fact that excitonic spectra details arise from atomic-scale contributions that must be integrated over a large spatial range containing a million and more of atoms. In this work we present a step-by-step solution to this problem: combined empirical tight-binding and configuration interaction scheme that unites linearly scaling computational time with the essentials of the atomistic modeling. We benchmark our method on the example of well-studied self-assembled InAs/GaAs quantum dot. Next, we apply our atomistic approach to crystal phase quantum dots containing more than 10 million atoms.

Accurate calculations of excitonic properties of semiconductor quantum dots must fulfill two apparently contradictory conditions. The first constraint is the necessity of handling computational domains containing millions of atoms. The second requirement is the atomistic accuracy necessary for the accurate description of the excitonic spectra. First principles modeling such as the density functional theory or GW-Bethe-Salpeter equation approach for self-assembled or nanowire quantum dots is still beyond the reach of modern computers. Continuous matter approaches like the effective mass approximation or k · p method have demonstrated the capability of describing main features in QDs; however, these methods are restricted by the resolution on the scale of a unit cell. One of the key examples is the bright exciton splitting where sophisticated multi-band approaches are needed to accommodate for the correct symmetry of the underlying crystal lattice. Apart from symmetry issues, even the most elaborate continuous matter tactics cannot fully account for effects of alloying lattice randomness, interface effects, or crystal phase symmetry, for which a truly atomistic approach is needed.

Practical methods, capturing atomistic structure of quantum dots and their surrounding matrix, include two semi-empirical approaches: the empirical tight-binding and the empirical pseudopotential method. Typical calculations using these approximate approaches involve three subsequent stages: a) calculation of equilibrium position of constituent atoms, b) calculation of quasielectron and quasihole states, and c) inclusion of excited quasiparticles interactions via screened Coulomb potential, solved by some sort of configuration interaction (exact diagonalization) method.

Although the stages of finding positions (strains) and quasi-particle calculations are often far from trivial, the key computational issue for approaches aiming to quantitatively describe nanosystem spectra is the ultimate step: the many-body calculation. This part of calculation is of particular importance as in a typical quantum dot photoluminescence experiment one does not observe the single-particle spectra, but rather many-body spectra of charged and neutral (multi-) excitonic complexes. Therefore in a realistic calculation the single particle part of the computation must be followed by a many-body calculation. Similarly to post-Hartree-Fock methods of quantum chemistry, the many-body calculation following the single-particle part is often the most time demanding stage of the entire empirical computations sequence. In particular, as a necessary prerequisite for the many-body calculation typically numerous two-particle integrals must be first calculated using quasiparticle functions. In the tight-binding (TB) approach, for N atoms, A basis functions per atom, and M quasiparticle states there are \(O(N^4A^2M^2)\) two-particle integrals, and the computational effort will thus formally scale as the fourth power in number of atoms, what leads to a practically untractable problem for typical quantum dots with numbers of atoms exceeding a million.

In this paper we present an approximated method for efficient order-N calculation of screened Coulomb and exchange integrals within the tight-binding framework. Apart from linear scaling our method accounts for terms that are customarily neglected in a typical tight-binding calculation of Coulomb matrix elements. We test our approach on the example of million-atom InAs/GaAs lens-shape self-assembled quantum dot and finally apply our approach to multi-million-atom crystal phase quantum dots.

I. COULOMB MATRIX ELEMENTS

At the moment one of the most successful empirical computational procedures is the empirical pseudopotential method. This approach uses “realistic” empirical pseudopotentials that reproduce correct band gaps and effective masses. Those potentials can be accommodated with a relatively small plane wave basis set and are used to obtain the single-particle eigenvectors as solution of the Schrödinger equation with an auxiliary basis set of strained Bloch function of the under-
lying bulk.\(^\text{34}\) Whereas conceptually straightforward, the practical implementation of the empirical pseudopotential method for quantum dots has been so far limited only to A. Zunger and co-workers.

On the contrary, numerous theoretical groups utilize different flavors of the empirical tight-binding method. The latter approach originates from the Slater-Koster scheme of orthogonal tight-binding\(^\text{35}\) whereas Hamiltonian matrix elements are given in terms of several empirical constants\(^\text{36}\) determined to reproduce bulk properties such as effective masses, bulk deformation potentials and gaps at different points of the Brillouin zone.\(^\text{37}\) Fitting process is usually far from trivial\(^\text{38}\); however, for a wide family of materials, there are reliable and accurate tight-binding parameter sets available in the literature.\(^\text{32,38}\)

The tight-binding method applied to a typical nanowire or self-assembled quantum dot problem produces a Hamiltonian of matrices of dimensions extending 10\(^8\); however, due to the nearest-neighbors approximation the Hamiltonian matrix is sparse. Then, for selected single particle states (close to energy band gap) the eigenproblem can be solved efficiently using e.g. Krylov iterative methods, such as Lanczos\(^\text{39}\) or Arnoldi\(^\text{40}\) algorithm, therefore resulting in a linear scaling of computational time with respect to the number of atoms in a computational domain. Like many other numerical approaches the empirical tight-binding benefits considerably from the parallelization that further reduces the overall computation time.\(^\text{41}\)

The tight-binding or linear combination of atomic orbitals (LCAO) wave function is given as:

\[
\psi(\vec{r}) = \sum_{\tilde{R}} \sum_{\alpha} b_{\tilde{R} \alpha} \phi_{\tilde{R} \alpha}(\vec{r} - \tilde{R})
\]

where the summation goes over all \((N)\) atoms \(\tilde{R}\) and all \((A)\) over atomic orbitals \(\alpha\) centered on a given atom, whereas \(b_{\tilde{R} \alpha}\) are basis expansion coefficients. Assuming a statically screened\(^\text{42}\) Coulomb interaction, the Coulomb matrix elements \(V_{ijkl}\) are given by\(^\text{32,33}\):

\[
V_{ijkl} = \int \int \psi^*_l(\vec{r}_1) \psi^*_j(\vec{r}_2) \frac{e^2}{\epsilon(\vec{r}_1, \vec{r}_2)} \psi_k(\vec{r}_2) \psi_l(\vec{r}_1)
\]

where \(\epsilon(\vec{r}_1, \vec{r}_2)\) is the position-dependent dielectric function and \(\psi\)'s are single-particle, electron or hole, wave functions. By substituting single-particle wave functions in form of Eq.\(^\text{4}\) into Eq.\(^\text{4}\) one obtains:

\[
V_{ijkl} = \sum_{\tilde{R}_1 \alpha_1} \sum_{\tilde{R}_2 \alpha_2} \sum_{\tilde{R}_3 \alpha_3} \sum_{\tilde{R}_4 \alpha_4} b_{\tilde{R}_1 \alpha_1}^* b_{\tilde{R}_2 \alpha_2}^* b_{\tilde{R}_3 \alpha_3} b_{\tilde{R}_4 \alpha_4} \times \omega(\tilde{R}_1 \alpha_1, \tilde{R}_2 \alpha_2, \tilde{R}_3 \alpha_3, \tilde{R}_4 \alpha_4)
\]

where four-fold summation goes over all atomic positions and orbitals and

\[
\omega(\tilde{R}_1 \alpha_1, \tilde{R}_2 \alpha_2, \tilde{R}_3 \alpha_3, \tilde{R}_4 \alpha_4) = \int \int \phi_{\tilde{R}_1 \alpha_1}(\vec{r}_1) \phi_{\tilde{R}_2 \alpha_2}(\vec{r}_2) \frac{e^2}{\epsilon(\vec{r}_1, \vec{r}_2)} \phi_{\tilde{R}_3 \alpha_3}(\vec{r}_2) \phi_{\tilde{R}_4 \alpha_4}(\vec{r}_1)
\]

is an integral calculated in a basis of tight-binding ("atomic") orbitals.

If treated directly, this procedure would result in \(O(N^4 A^4)\) terms (atomic integrals) constituting one quasi-particle Coulomb matrix element, where \(N\) is the number of atoms in the domain (typically \(N \sim 10^6\) for self-assembled and nanowire quantum dots) and \(A\) is number of (spin-)orbitals associated with each of atoms (e.g. 20 for the \(sp^3d^5s^2\) TB model\(^\text{42}\)). To further complicate matters, practical calculation demands computation of both one, but numerous electron-electron, electron-hole, and electron-hole Coulomb matrix elements calculated using Eq.\(^\text{4}\). For example, in a typical quantum dot calculation involving 12 electron states and 12 hole states (including spin), the total number of these quasi-particle Coulomb matrix elements reaches 10\(^5\), whereas in certain situations\(^\text{42}\) number of quasi-particle states \((M)\) used for the calculation must be further extended. Either way, the overall computation time scales as \(O(N^4 A^4 M^4)\).

Typically, this formidable problem is resolved by utilizing a series of approximations\(^\text{42,43}\) including neglect of three- and four-center integrals \(\omega\). Further approximations involve multi-pole expansion of single integral \(\omega\) and retaining monopole-monopole contributions only\(^\text{32,33}\).

Finally one gets an approximate form of Coulomb matrix elements\(^\text{42}\):

\[
V_{ijkl} = \sum_{\tilde{R}_1} \sum_{\tilde{R}_2} \left[ \sum_{\alpha_1} b_{\tilde{R}_1 \alpha_1}^* b_{\tilde{R}_2 \alpha_1} \right] \left[ \sum_{\alpha_2} b_{\tilde{R}_2 \alpha_2}^* b_{\tilde{R}_3 \alpha_2} \right] \frac{e^2}{\epsilon(\tilde{R}_1 - \tilde{R}_2)} \sum_{\alpha_3} b_{\tilde{R}_3 \alpha_3}^* b_{\tilde{R}_4 \alpha_3} \omega(\tilde{R}_1 \alpha_1, \tilde{R}_2 \alpha_2, \tilde{R}_3 \alpha_3, \tilde{R}_4 \alpha_4).
\]

where the first term is the long-range, bulk-screened, contribution to the two-center integral built from the monopole-monopole interaction\(^\text{44,45}\) of two charge densities localized at different atomic sites. The second term is the on-site unscreened part, calculated by direct integration using atomic orbitals.\(^\text{32,33}\) This approach is justified by the fact that the screening (Thomas-Fermi) radius \((\approx 2-4\,\text{Å})\) is on the order of a bond length\(^\text{15,29}\) resulting in nearly bulk screening of off-site (long-range) terms and limited screening of on-site (short-range) terms contribution. A potential problem arising here is the choice of atomic basis used for calculation of \(\omega\) on-site integrals. The generally important matter of basis dependence will be discussed later in more detail.

The second summation in Eq.\(^\text{4}\) over on-site terms can be further simplified by neglecting exchange terms and multiple \(\omega\)'s replaced by a single on-site contribution\(^\text{42}\):

\[
V_{ijkl} = \sum_{\tilde{R}_1} \sum_{\tilde{R}_2} \left[ \sum_{\alpha_1} b_{\tilde{R}_1 \alpha_1}^* b_{\tilde{R}_2 \alpha_1} \right] \left[ \sum_{\alpha_2} b_{\tilde{R}_2 \alpha_2}^* b_{\tilde{R}_3 \alpha_2} \right] V_{\tilde{R}_1 \tilde{R}_2} \times \frac{e^2}{\epsilon(\tilde{R}_1 - \tilde{R}_2)} \sum_{\alpha_3} b_{\tilde{R}_3 \alpha_3}^* b_{\tilde{R}_4 \alpha_3} \omega(\tilde{R}_1 \alpha_1, \tilde{R}_2 \alpha_2, \tilde{R}_3 \alpha_3, \tilde{R}_4 \alpha_4)
\]

where the on-site atomic contribution \(U_{\tilde{R}}\) can be calculated (estimated) using different approaches.\(^\text{15,29}\)
Whereas relatively uncomplicated, Eq. 5 and Eq. 6 give reasonable agreement with the experiment and other computational approaches. The above procedures (Eq. 5 and Eq. 6) give also far more approachable $O(N^2)$ scaling of a single Coulomb matrix element calculation rather than impractical $O(N^3)$ of the straightforward method (Eq. 3). Further reduction of the computational time (but not the scaling factor) can be achieved by utilizing multi-scale approaches (i.e., using smaller domains at different stages of the computation). While not affecting the scaling properties, the usage of numerical libraries such as BLAS can further reduce the computation time by avoiding time consuming recalculation of intermediate terms.

Apart from the advantages, the above methods (Eq. 5 and Eq. 6) reveal two apparent issues. The first is a non-linear $O(N^2)$ scaling of the computational time leading to exploding computational complexity for domains containing millions of atoms. The second problem is an possible inaccuracy related to the two-center and the monopole-monopole approximations.

II. WAVE-FUNCTION RECONSTRUCTION

In what follows we present a numerical method that effectively addresses above issues. Let us starts by reiterating that the LCAO representation of the tight-binding wavefunction leads to a non-linear scaling of the two-particle Coulomb matrix elements calculation with respect to the number of atoms in the domain. Therefore, after TB stage of calculation, we convert TB eigenstates from a typical LCAO wave-functions to a real-space tight-binding wave-function representations. This stage is achieved by an introduction of a three dimensional, uniform real-space grid with complex values. At each point of the spatial grid we use Eq. 1 (assuming particular basis set) to calculate the wave-function values. We repeat this procedure and process in this way each point of the spatial grid we use Eq. 1. More strictly, rather than due to orthogonality, this assumption originates from atomic orbitals spatial locality, i.e., relatively small spatial extent of atomic orbitals when compared to dimensions of the entire system. Similar assumptions are typically utilized in the context of other linear-scaling approaches that rely heavily on the use of strictly confined basis orbitals, i.e., orbitals zeroing beyond a certain radius. One way of achieving this goal is the method of Sankey and Niklewski where the (pseudo-) atom is embedded within a spherical box of finite radius.

Should $R_{cut}$ be much smaller then the system size then the number of atoms ($N_{cut}$) within the cut-off radius: $N_{cut} \ll N$. More importantly, for quantum dots embedded in bulk-like matrix, $N_{cut}$ should be relatively constant and independent from $N$, leading to $O(N)$ scaling of the tight-binding wave-function reconstruction time.

A straightforward implementation of Eq. 7 would involve iteration over grid points and therefore implicitly perform costly calculations of distances between all grid points and all atoms. Instead, in our implementation, we iterate over all atoms and update only grid points within a neighborhood defined as a cube of edge length equal to $2R_{cut}$. This procedure can also be efficiently parallelized.

In case of semiconductor quantum dots above assumptions and exact value of $R_{cut}$ will be verified later by numerical tests. The size of the reconstruction grid should be equal to spatial system dimensions increased in all directions by necessary margins equal to $R_{cut}$. We also note that we separately compute and store spin-up and spin-down wave-function components at each grid point. Once the reconstruction is finished, the wave-function is finally renormalized on the grid.

With the TB wave-function given in real-space we can follow with the calculation of Coulomb matrix elements using Eq. 2. Straightforward substitution of real-space wave-functions into Eq. 2 and direct integration would however lead to $O(P^2) \propto O(N^2)$ complexity. Fortunately, this equation be conveniently evaluated in the reciprocal space. Eq. 2 can be cast in a general form:

$$V_{ijkl} = \int \int \rho_{il}(\vec{r}) G(\vec{r} - \vec{r}') \rho_{jk}(\vec{r}') dV dV',$$  \hspace{1cm} (8)$$

where $ho_{il} = \psi_i^* \psi_l$, $\rho_{jk} = \psi_j^* \psi_k$ and $G(\vec{r} - \vec{r}')$ is the screened Coulomb interaction. Then, potential $V_{ij}$ cal-
culated from quasi-density $\rho_{jk}$ is given as:

$$V_{jk}(\vec{r}) = \int G(\vec{r} - \vec{r}') \rho_{jk}(\vec{r}') dV'$$

(9)

For a discrete case, assuming regular grid with the grid step $h$, we obtain:

$$V_{jk}[\vec{r}] = \sum_{\vec{r}'} G(\vec{r} - \vec{r}') \rho_{jk}[\vec{r}'] h^3 = (G \ast \rho_{jk})[\vec{r}] h^3$$

(10)

where $\vec{r}$ and $\vec{r}'$ are points on a discrete grid and $(G \ast \rho_{jk})$ is a full convolution between quasidensity $\rho_{jk}$ and the screened Coulomb interaction $G(\vec{r} - \vec{r}')$, which is defined on a three-dimensional domain twice as large as $\rho_{jk}$ (as it includes both positive and negative shifts) in every dimension. Therefore, the density grid must also be padded with zeros, resulting in $8P$ grid points instead of $P$. Due to this padding, the full convolution $(G \ast \rho_{jk})$ is equivalent to the circular convolution, which in turn can be effectively computed using Fast Fourier Transform (FFT) algorithm\textsuperscript{22} in $O(P \log P)$ time.

Since we use FFT purely as a computational tool to calculate full (not circular) convolution, we do not introduce any undesired periodicity to the problem. Details of this approach are given e.g. in Ref.\textsuperscript{22}. This technique is a standard in digital signal processing for a discrete Fourier transform treatment of non-periodic signals convoluted with a response function of a finite duration. Otherwise, Eq.\textsuperscript{10} would typically converge slowly with respect to the grid (supercell) volume. Different techniques including multi-pole expansion\textsuperscript{30,31,32} or truncated Coulomb interaction\textsuperscript{17} would be typically necessary to speed up this convergence.

The method we utilize seems not to be often used in the electronic structure calculation, most likely due to the increased memory demand. In our case the size of the FFT domain is effectively doubled in all three directions. As a practical benefit, we do not need to perform convergence tests with respect to the domain size as Eq.\textsuperscript{11} gives exactly the same results as the direct integration of Eq.\textsuperscript{2}. In the latter part of the text we will additionally verify that statement by performing numerical tests of the effective range of the Coulomb interaction. We also note that in other approaches the size of the supercell is often much larger then the actual system size\textsuperscript{22}. Moreover, extending the FFT domain is not affecting the time needed for the wave-function reconstruction, but only the (relatively short) time of the FFT calculation.

$V_{ijkl}$ is finally given as a straightforward $O(P) \propto O(N)$ summation over all grid points:

$$V_{ijkl} = \sum_{\vec{r}} \rho_{ilk}[\vec{r}] V_{jkl}[\vec{r}] h^3$$

(11)

For a given $jk$ pair of tight-binding (grid reconstructed) functions, $V_{jk}$ and the FFT transform are calculated only once and are used to calculate all resulting Coulomb matrix elements $V_{ijkl}$, therefore avoiding costly recalculation of $V_{jk}$.

Our approach accounts for dielectric effects at different levels of approximation. For example, we can use any form of distance dependent dielectric function, e.g. a Thomas-Fermi model of Resta\textsuperscript{68,69} customarily utilized in the empirical-pseudopotential method calculations.\textsuperscript{68,69} Apart from the distance-dependence, we can account for the spatial dependence of the dielectric medium. Details of this latter approach will be discussed elsewhere. In the current paper $G$ is either taken as a Fourier transform of Coulomb bulk-screened interaction or is given by a Thomas-Fermi model of Resta.\textsuperscript{68,69} Finally, we note that due to introduction of large spatial grid our method demands substantially larger computer memory than the simple model (Eq.\textsuperscript{5}).

### III. Lattice and the Single Particle Spectra

As discussed in the introduction, the calculation consists of several major steps: first atomic positions are calculated. For lattice mismatched system (such as InAs/GaAs quantum dots) to calculate strain relaxed positions we use the atomistic valence force field (VFF) approach of Keating.\textsuperscript{66,67} This method is described in more detail in Ref.\textsuperscript{68,69} and in our previous papers.\textsuperscript{4,5,14,15} We note here only that the VFF approach is a $O(N)$ method and can be efficiently parallelized allowing for treatment of domains containing $10^8$ atoms.\textsuperscript{68} For InP crystal phase quantum dots, we neglect strain effects.\textsuperscript{26,27}

Once the atomic positions are given, we use them to calculate single particle energies with the empirical nearest-neighbor tight-binding model that accounts for strain, spin-orbit interactions, crystal lattice symmetry, and wurtzite crystal field splitting in case of zinc-blende/wurtzite mixed crystal phase quantum dots.\textsuperscript{4,5,14,15}

The single-particle tight-binding Hamiltonian for the system of $N$ atoms and $m$ orbitals per atom can be written, in the language of the second quantization, in the following form:

$$\hat{H}_{TB} = \sum_{i=1}^{N} \sum_{\alpha=1}^{m} E_{i\alpha} c_{i\alpha}^+ c_{i\alpha} + \sum_{i=1}^{N} \sum_{\alpha=1,\beta=1}^{m} \lambda_{i\alpha,\beta} c_{i\alpha}^+ c_{i\beta}$$

$$+ \sum_{i=1}^{N} \sum_{j=1}^{4} \sum_{\alpha,\beta=1}^{m} t_{i\alpha,j\beta} c_{i\alpha}^+ c_{j\beta}$$

(12)

where $c_{i\alpha}^+$ ($c_{i\alpha}$) is the creation (annihilation) operator of a carrier on the orbital $\alpha$ localized on the site $i$, $E_{i\alpha}$ is the corresponding on-site (diagonal) energy, and $t_{i\alpha,j\beta}$ describes the hopping (off-site, off-diagonal) of the particle between the orbitals on (four) nearest neighboring sites. Coupling to further neighbors is neglected, whereas $\lambda_{i\alpha,\beta}$ (on-site, off-diagonal) accounts for the spin-orbit interaction following the description given by Chadi.\textsuperscript{17}

For InAs/GaAs system we use tight-binding parameters set from Ref.\textsuperscript{25} in $sp^3d^5s^*$ parametrization. More
details of the $sp^3d^5s^*$ tight-binding calculation were discussed thoroughly in our earlier papers.\textsuperscript{24,25}

For InP crystal phase quantum dots we have used Vogl et al.\textsuperscript{27} $sp^3s^*$ tight-binding parameters augmented to account for the spin-orbit splitting (126 meV). We have additionally modified these parameters to account for the increased wurtzite’s band gap (1.474 eV)\textsuperscript{28} between the wurtzite and zinc blende segments, and the wurtzite crystal field splitting (26 meV)\textsuperscript{29}. The tight-binding parameters used in the calculation for both phases are summarized in Table I.

For million-atom systems the size of the tight-binding Hamiltonian\textsuperscript{30,31} typically exceeds $10^7$, reaching $10^8$ for the largest crystal phase quantum dot considered in this work. However, due to the nearest-neighbor approximation, the Hamiltonian matrix is sparse and the number of non-zero matrix-elements scales as $O(N)$. Hamiltonian elements are calculated on-demand without occupying computer’s memory. Several lowest electron and hole states are found by means of Lanczos algorithm with matrix-vector multiplication parallelized using the MPI library. We reiterate that thanks to the application of Lanczos algorithm, and the sparse form of Hamiltonian, the process of partial Hamiltonian diagonalization scales linearly with the domain size. More details will be shown in the following section.

IV. BENCHMARKS

Once single-particle states are calculated, we move to the efficient calculation of Coulomb matrix elements. We first illustrate our method on the example of “standard”\textsuperscript{31,32} lens-shaped InAs/GaAs quantum dot. The quantum dot has a diameter of 25 nm and a height of 3.5 nm and is located on a 0.6 nm thick wetting layer. The InAs quantum dot and the wetting layer are embedded into GaAs matrix, with the total number of atoms in the tight-binding computational domain reaching $0.6 \times 10^6$ atoms. This “standard” quantum dot will be used to benchmark our approach, while later in the paper we will present results for InP crystal phase quantum dots.

In the tight-binding method the Hamiltonian matrix elements are treated as empirical parameters and the basis is not explicitly specified. Due to this freedom there are several practical choices possible for the basis functions. These typically include Slater orbitals\textsuperscript{29,73} and Herman-Skillman orbitals.\textsuperscript{74,75} Slater-type orbitals are defined by simple rules giving approximate analytic atomic wave functions, in form of $\phi_\mu = N_\mu Y_\mu(\theta, \phi) r^{n-1} e^{-\alpha r}$, where $n$ is the principal quantum number, $N_\mu$ is the normalization constant, $\mu$ denotes orbital symmetry, and $Y_\mu(\theta, \phi)$ corresponding spherical harmonic, finally $\alpha$ is a screening constant obtained by a set semi-empirical principles. On the other hand, Hermann-Skillman orbitals are be obtained by self-consistent numerical calculations for free atoms and ions.

Importantly, we note here that there is ongoing research for new tight-binding schemes\textsuperscript{26,76} that would remove the basis ambiguity and directly relate tight-binding parameters with a well defined orbital set.

Slater orbitals have analytical formulation, however Hermann-Skillman orbitals should correspond more closely to the actual atomic states. None of these basis sets is orthogonal (due to non-zero overlaps between orbitals on neighboring atoms), as assumed by the Slater-Koster tight-binding approach, however Hermann-Skillman orbitals are also better localized in space (Fig. 1) and have smaller overlap between neighboring sites, whereas Slater orbitals have tails extending over many lattice sites.

Our implementation accepts any form of orbitals defined as a product of radial and angular parts, whereas the radial part can be given by an analytical or numerical form. Therefore our method can, in principle, utilize orbitals such as those generated by TB-DF approach\textsuperscript{77}, or new schemes of empirical tight-binding parameterization\textsuperscript{76,77}.

Figure 2 shows electron-electron $J_{ee}$, electron-hole $J_{eh}$ and hole-hole $J_{hh}$ Coulomb integrals for electron and hole occupying their ground $s$ state\textsuperscript{35}, calculated as a function of wave-function reconstruction cut-off radius using Herman-Skillman basis, grid step $\Delta = 0.8$ Å, and Thomas-Fermi screening model for a lens-shaped InAs/GaAs quantum dot. Here we use notation, where e.g. $J_{eh} \equiv V_{c_1 h_1 c_1} \equiv (c_1 h_1 c_1)$. These three integrals are of particular importance as they allow to esti-
mate the single exciton and excitonic complexes binding energies at the level of Hartree-Fock approximation. Figure 2 shows that the cut-off radius of \( \approx 1.5 \) nm is sufficient for the converged (within 0.1\% accuracy) calculation of these Coulomb integrals. We performed numerical tests for numerous quantum dot systems (including nanocrystals, self-assembled and nanowire quantum dots) and generally found that the cut-off radius of 1.5–2.0 nm for Herman-Skillman, and 2.0–2.5 nm for Slater orbitals, is sufficient to achieve this level of accuracy. We also found that the cut-off radius is, to a large degree, independent from the size and shape of the investigated nanosystem.

We note as well that there are \( \approx 500 \) atoms within 1.5 nm cut-off radius, potentially contributing to a single grid point. As discussed earlier this is a much smaller number than total \( \approx 10^6 \) number of atoms in the computational domain. Therefore without the \( R_{\text{cut}} \) optimization (Eq. 7), the reconstruction stage would take \( 10^3 \) times longer, rendering the entire calculation impractical.

Figure 3 shows the evolution of the same Coulomb integrals for the same quantum dot system as discussed earlier (using Herman-Skillman orbitals as well) however as a function of the grid spatial resolution and assuming a fixed cut-off radius equal to 1.5 nm. For large grid steps there are noticeable oscillations related to the overlap of the regular computational grid and the underlaying zinc-blende crystal lattice. These oscillations are particularly pronounced at the grid spacings 0.2–0.3 nm comparable to typical InAs and GaAs bond-lengths, however for a grid step \( h \) lower than 0.09 nm integral values stabilize. Importantly, already for \( h \approx 0.1 \) nm the relative uncertainty due to grid spacing errors is \(<1\%\). We checked that these conclusions can be generalized to all other integrals entering the excitonic calculation. Unless specified otherwise, the results presented below refer to the \( h = 0.08 \text{ nm} = 0.8 \text{ Å} \) grid step. Further increase of grid resolution (decrease of \( h \)) seem unnecessary as excitonic properties of quantum dots are determined by contributions from valence orbitals rather the subatomic details of atomic cores.

For \( h \approx 0.1 \) nm there is about 100 grid points per atom, each point storing spin-up and spin-down part of the wavefunction. For comparison, in the LCAO form and \( sp^3d^5s^* \) parameterization there are 20 spin-orbitals per atom and therefore 20 (complex) expansion coefficients per single atom. Therefore we note the memory needed to store the wave-function in the real-space representation is increased by factor \( \approx 10 \) (20 for \( sp^3s^* \)) when compared to the conventional TB-LCAO form. For a million-atom system this corresponds to \( \approx 3 \) GB per single TB wavefunction and can be efficiently handled by

| \( E_{\text{cut}} \) | \( E_{\text{sp}} \) | \( E_{\text{pa}} \) | \( E_{\text{ss}} \) | \( E_{\text{eh}} \) | \( E_{\text{eh}} \) | \( V_{\text{ee}} \) | \( V_{\text{eh}} \) | \( V_{\text{hh}} \) | \( V_{\text{hh}} \) | \( V_{\text{sa}} \) | \( V_{\text{sc}} \) | \( V_{\text{sa}} \) | \( V_{\text{pc}} \) | \( \lambda_{\text{s}} \) | \( \lambda_{\text{c}} \) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| ZB | -8.5274 | 0.7677 | 0.7677 | -1.4826 | 3.9407 | 3.9407 | 8.2635 | 7.0665 | -5.3614 | 1.8801 | 4.2324 | 4.2324 | 0.067 | 0.067 | 0.392 |
| WZ | -8.4634 | 0.8323 | 0.8063 | -1.4826 | 3.9407 | 3.9407 | 8.2635 | 7.0665 | -5.3614 | 1.8801 | 4.2324 | 4.2324 | 0.067 | 0.067 | 0.392 |
modern day computers. To summarize, the cut-off radius of about 2 nm and grid-step of about 0.1 nm were found satisfactory for the reasonable convergence of selected Coulomb matrix elements.

Table I shows various Coulomb direct and exchange integrals calculated for InAs/GaAs lens-shaped quantum dot ($D = 25$ nm, $h = 3.5$ nm) using different approaches. For this particular nanosystem the electron-electron repulsion has larger magnitude than electron-hole attraction or hole-hole repulsion. In all considered cases there is only a minor difference due to dielectric screening model used in a calculation. This confirms our general conclusion that Coulomb interactions in typical self-assembled quantum dots are nearly bulk screened as discussed earlier in the text. For the case of $J_{ee}$ all approaches give similar value of 25–26 meV. There is, however, a substantial discrepancy between different approaches for direct integrals involving hole states, i.e. $J_{hh}$ and $J_{hh}$. This is particularly noticeable for $J_{hh}$≈17.5 meV obtained using Slater-type orbitals, whereas both Herman-Skillman orbitals and the simple model of Eq. (4) predict $J_{hh}$ to vary between 20.5 and 21.25 meV.

The above differences can be understood in terms of atomic orbitals contributions to single particle states. Whereas, the ground electron and hole states have quite similar envelopes, they have much different (s- and p-type correspondingly) dominant orbital contributions. In particular, p-type (and d-type) Slater-type orbitals are typically substantially more delocalized in space than corresponding Herman-Skillman orbitals. Therefore the difference between both basis sets is due to spatial extent of basis orbitals, what will be verified later in the text.

Apart from Coulomb direct integrals, Table I shows three selected exchange integrals. Those integrals play important role in the control of quantum dot excitonic fine structure. The dark-bright exciton exchange splitting is determined predominantly by a (real) exchange matrix element, which also conserves spin: $\langle e_{\uparrow} h_{\uparrow} e_{\downarrow} h_{\downarrow} \rangle$, whereas $\langle e_{\downarrow} h_{\downarrow} e_{\uparrow} h_{\uparrow} \rangle$ is responsible for mixing of two bright-excitonic states ($e_{\uparrow} h_{\uparrow}$ and $e_{\downarrow} h_{\downarrow}$) and therefore leads to the bright-exciton splitting. Finally $\langle e_{\uparrow} h_{\downarrow} e_{\downarrow} h_{\uparrow} \rangle$ mixes two dark states ($e_{\uparrow} h_{\downarrow}$ and $e_{\downarrow} h_{\uparrow}$) and leads to the dark-exciton splitting. In all above cases we used notation where $e_{\uparrow}$ and $h_{\uparrow}$ is a Kramers degenerate pair of states corresponding to the electron ground state energy. Analogous notation has been used for hole states as well.

For the case of exchange integrals the effect of the basis has very noticeable consequences. Again, whereas results obtained using Herman-Skillman orbitals and Eq. (4) agree reasonably, especially for the electron-hole exchange ($\approx 0.25$ meV), the value calculated by using Slater-type orbitals is about three time larger and close to 0.8 meV. Even larger difference is reported for integrals related to the bright-exciton splitting (anisotropic electron-hole exchange) and the dark-exciton splitting. In this case the Slater-type orbitals basis overestimates the other two approaches by more than an order of magnitude. It should be noted that the bright-exciton splitting (fine structure splitting) for cylindrical (or close to cylindrical) quantum dots observed in the experiment is typically on the order of 10 to 100 $\mu$eV, therefore in clear disagreement with the approach using Slater-type orbitals.

To study this effect further, Figure 4 shows the same integrals as presented in Table I however calculated as a function of the Coulomb interaction radius which can be artificially limited to a certain radius $r_{\text{max}} \equiv \max|\vec{R} - \vec{R}'|$. In this case for a simple model, Eq. (4) is simply replaced with the following formula:

$$V_{nn} = \begin{cases} U_n & : n = m, \\ \frac{1}{\epsilon|\vec{R}_n - \vec{R}_m|} & : n \neq m \land |\vec{R}_n - \vec{R}_m| \leq r_{\text{max}}, \\ 0 & : n \neq m \land |\vec{R}_n - \vec{R}_m| > r_{\text{max}}. \end{cases}$$

(13)

Whereas for grid calculations, in order to avoid granularity artifacts we use the sigmoid-type function:

$$G(\vec{r}) = \frac{\epsilon^2}{4\pi\lambda^2} \left(1 + e^{-\lambda(|\vec{r}|-r_{\text{max}})}\right)^{-1},$$

(14)

where $\lambda > 0$ plays a role of a smoothing parameter. For clarity we emphasize that the Coulomb interaction cut-off radius is a different quantity from the wave-function reconstruction cut-off radius studied in Fig. 2.

For all considered integrals their values stabilize for the Coulomb interaction cut-off radius $\approx 20$ nm comparable to the quantum dot diameter. This further proves that the calculation is free from any effects of the image charges. Fig. 4 (upper row) demonstrates rather small contributions to the direct matrix elements for this nanosystem that originate from on-site and nearest-neighbor contributions, and that these integrals are dominated by the long-range contributions. Interestingly, for the case of exchange integrals there are noticeable maxima in their modulus at about 8–10 nm, corresponding
TABLE II. Selected Coulomb and exchange integrals calculated for lens-shaped (see the text) InAs/GaAs quantum dot for different basis and two different models of dielectric screening: bulk-like $\epsilon_{InAs}$, screening and Thomas-Fermi (T-F) model of model (TB-LCAO; Eq. 5) are shown for comparison.

|                        | STO | H-S orbitals | TB-LCAO | Opt. STO |
|------------------------|-----|--------------|---------|----------|
| $J_{HH} = (\epsilon_1 \epsilon_1 \epsilon_1 \epsilon_1)$ [meV] | 20.60 | 26.05 | 24.61 | 24.65 | 24.75 | 25.82 |
| $J_{HH} = (\epsilon_1 h_1 h_1 \epsilon_1)$ [meV] | 20.03 | 20.06 | 21.96 | 21.99 | 22.54 | 22.66 |
| $J_{hh} = (h_1 h_1 h_1 h_1)$ [meV] | 17.54 | 17.58 | 20.41 | 20.47 | 21.25 | 20.81 |
| $\langle \langle \epsilon \epsilon h \epsilon h \rangle \rangle$ [\mu eV] | 708.5 | 722.8 | 233.5 | 254.9 | 238.6 | 154.2 |
| $\langle \langle \epsilon \epsilon h \epsilon h \rangle \rangle$ [\mu eV] | 553.8 | 555.9 | 50.1 | 49.7 | 22.5 | 20.8 |
| $\langle \langle \epsilon \epsilon h \epsilon h \rangle \rangle$ [\mu eV] | 13.4 | 13.5 | 0.6 | 0.6 | 0.2 | 0.6 |

As discussed earlier, in case of semiconductor quantum dots, one could assume that for sites which are far enough apart from each other the exact structure of the localized orbitals is not important\(^{23}\) and that the long-range contributions are dominated by the monopole-monopole interaction of two charge densities localized at different sites. This assumption is clearly not fulfilled for Slater-type orbitals which extend over many lattice constants from the site center. This is especially important for the bright-exciton splitting that has been shown to be strongly related to the (local) electron-hole non-orthogonality on the scale of a unit cell.\(^{25,26}\) Slater-type orbitals localized on neighboring sites, i.e. within the same unit cell, are clearly (Fig. I) far from orthogonal, resulting in strongly overestimated value of anisotropic exchange integral.

In order to study these effects further, we note that bulk on-site atomic energies are shifted with respect to their free atom counterparts.\(^{47}\) By the same token, the spatial extent of basis orbitals in bulk should be reduced as compared with free atoms. This claim has been recently supported by work by Benchamekh et al.\(^ {28}\) where microscopic (Bloch) functions for tight-binding model where obtained by a process in which screening constants $\alpha$ of Slater-type orbitals were optimized by the fitting. Ref.\(^{26}\) shows that the fitting procedure has relatively small effect on well localized $4s$ and $4p$ orbitals ($sp^3$ in tight-binding), e.g. altering $4s$ screening constant from 1.7 to 1.94. On the other hand, the screening constant of Slater-type $4d$ arsenic orbital is increased significantly from 0.27 in free atom case to 0.96 for arsenic site in GaAs bulk crystal. The screening constant of $5s$ (i.e. $s^*$) orbital is affected even more, being increased from 0.4 to over 1.74 for the bulk case. This effectively corresponds to effective “compression” of atomic orbitals in bulk, and is especially pronounced for higher orbitals of the largest spatial extent. These results indicate strong (exponential) dumping of atomic orbital tails at long distance as compared to free atoms counterparts, what is apparent radial density plot as seen on Figure 5. This procedure reduces significantly basis functions tails and the contribution from a given site is on average effectively limited to the radius of about 1 nm.

Whereas modified screening constants are currently not available for indium arsenide, we repeated our calculations using an approach in which we increased screening constants on $s$, $p$, $d$, and $s^*$ orbitals all atomic species in the nanosystem by the following values: 0.36, 0.25, 0.7, 1.3. These values are close to modifications reported by Ref.\(^ {26}\). Results of our calculations are shown on the right-hand column (Opt. STO) in Table II.

In the optimized case Coulomb and exchange integrals are similar to those given by a more confined Herman-Skillman basis or the asymptotic model of
FIG. 6. Band alignment of InP zinc-blend and wurtzite used in our calculations, and schematics of the system.

Eq. (TB-LCAO). This is particularly pronounced for exchange integrals, e.g. for $|\langle e^\uparrow h^\downarrow \mid e^\downarrow h^\uparrow \rangle|$ (related to the bright-exciton splitting) where the “compressed” Slater-type orbitals give values order of magnitude smaller than unmodified orbitals and very close to that of Eq. Otherwise, we note that the choice of unmodified Slater-type basis results in severe overestimation of above integrals due to the overlap of orbitals between far (> 1.0 nm) neighbors.

V. CRYSTAL PHASE QUANTUM DOTS

Crystal phase quantum dots gained recently a lot of attraction due to nearly perfect interface between crystal phases constituting the system, well defined (with monolayer accuracy) height, and the lack of alloying effects pestering spectral reproducibility of typical self-assembled quantum dots. In this section we apply our method to a single InP crystal phase quantum dot. We model this nanostructure by a zinc-blende InP segment of 1 nm height (3 monolayers, single ABC stacking sequence) along the [111] direction, embedded between two 30 nm (100 MLs) long wurtzite InP segments grown along [0001] direction. Fig. shows corresponding energy band alignment of the studied system, plotted along the growth axis, and schematics of the nanosystem. The total height of the system exceeds 60 nm, whereas we vary nanowire diameter from 12 to 70 nm, therefore a number of atoms in the system varies from close 0.3 to over 10 million atoms.

Fig. shows the effective single particle gap (defined as the energy difference between ground electron and hole state) calculated for the crystal phase quantum dot as a function of a diameter. Importantly, the effective gap varies substantially from over 1.5 eV for the lowest considered diameter (11.7 nm) to $\approx 1.46$ eV for the largest considered diameter of 70.4 nm. This results shows that it is in principle possible to tailor the effective gap of these nanostructure by control of a nanowire diameter. On the other hand, Fig. reveals the significant role of lateral confinement, therefore without precise control of diameter crystal phase quantum dots are subject to a potential spectral inhomogeneity.

Fig. shows the time of the single particle (tight-binding) part of calculation as function of number of atoms (which is growing quadratically with the nanowire diameter). Each of the computations were performed on the same 48-core computer system. The time of the
computation scales practically linearly as a function of number of atoms. The small steps on the plot are related to parallel computation and load-balancing issues, i.e. problem of uniform division of a discrete atomic grid to a discrete number of processors.

As mentioned in the introduction, experimental spectra are obtained for the interacting electron-hole pair, i.e. exciton. Therefore we follow our single-particle calculation with a many-body configuration interaction (CI) calculation. We performed our calculations using two approaches, first is the traditional TB-LCAO method of Eq. 6 that involved \( O(N^2) \) summations, and the second is our linear-scaling approach. In order to execute this comparison we have utilized a limited CI basis involving lowest three (with spin, six) electron states and lowest four (with spin, eight) hole states. For each diameter, we have calculated the total of 1296 electron-electron integrals, \( 2 \times 2304 = 4608 \) electron-hole Coulomb and exchange integral, and 4096 hole-hole integrals. Note: Number of integrals to be calculated is effectively reduced by a factor of four due to the symmetries of Coulomb matrix elements. Computation of these integrals is a prerequisite not only for the single exciton calculations (which involve only electron-hole interactions), but also for other excitonic complexes such as a biexciton (that additionally needs electron-electron and hole-hole integrals). In particular, the above basis results in total 48 configurations for the single exciton and 420 configurations for the biexciton. Such number of configurations presents little computational effort for the CI Hamiltonian diagonalization; however, due to rapidly (\( M^4 \)) increasing number of Coulomb matrix elements, further increase of the CI basis would result in prohibitive computational times for the method of Eq. 6 and would render the comparison between methods impractical.

Fig. 9 shows the excitonic binding energy for the discussed crystal phase quantum dot as a function of diameter. The exciton binding energy is defined as an energy difference between the ground state of the interacting electron-hole pair and the single particle gap studied earlier. With the increasing of diameter, the magnitude (absolute value) of the binding energy decreases from a high-lateral confinement regime (\( \approx 14 \) meV) for small diameters, to nearly bulk-like binding energy of \( \approx 6 \) meV for the largest diameter. This figure reveals a transition from quantum dot-like to a quantum well-like confinement for large diameter systems. The unexpected steps (e.g. 33 nm) in otherwise monotonous function are an artefact of a limited (not converged) configuration interaction basis set. Most importantly, we note that in the range where both methods can be compared with each other (\( d < 50 \) nm) they produce practically identical output. We note as well the results shown here were obtained on a grid step of 1.0 Å, yet they differ only by a tiny fraction of a meV (typically 0.05 meV) from results obtained on the 0.8 Å grid. Additionally, we point that due to \( C_{3v} \) symmetry crystal phase quantum dots have exactly vanishing excitonic fine structure\(^6\) as confirmed by our studies, therefore these systems are to a large degree free from basis dependence artifacts mentioned earlier.

Whereas the excitonic results reported by both methods are nearly identical, the cost of the computational differs dramatically as shown on Fig. 10. With the domain size growing from 0.28 to 4.5 million atoms, the time spend in Eq. 5 calculation is increased by more than \( \approx 460 \) times, showing strong non-linear scaling. This scal-
were obtained for grid spacing where the number of atoms in the domain. The time and memory demand is increased, e.g. by \( \approx 30 \) factor, corresponding to similar growth of the number of atoms in the domain. The timings presented on Fig. 11 were obtained for grid spacing equal to 1 Å. We note that for higher resolution grids the time and memory demand is increased, e.g. by \( \approx 40\% \) factor for the 0.9 Å grid spacing.

In principle, a further speedup could be achieved: both results were obtained on the same 240-core computer cluster system, however the FFT part of the calculation where run on 48 cores only, due to the limited scaling of the FFT algorithm (as implemented in the FFTW library, which we have used in this work). Artifacts of the FFT parallelization are well visible on Fig. 11 where the total time of the calculation in our approach was divided into the contribution from the reconstruction part and the FFT step of the computations. The reconstruction itself scales practically linear as function of number of atoms and in fact the overall time is dominated by this stage. Noticeable steps in time dependence of the FFT part are related to a) additional padding of the reconstruction domain, to ensure good performance of the FFT, and b) the load balancing issues on parallel computer system. In fact, the FFT time spent in 10-million case is smaller than in 7-million case, as the grid in the larger case can be more efficiently divided by the number of processors.

We have checked that quasi-linear scaling properties of our approach are not limited to this particular system, but instead, it is a general feature, with similar scaling properties for various nanosystems such as: nanocrystals, nanowires, self-assembled and nanowire quantum dots.

![Graph](image_url)

**FIG. 11.** Times of the grid reconstruction and the FFT stages (see the text) versus the total time of the computation.

We have presented a method for an efficient, order-\( N \) calculation of excitonic spectra of semiconductor nanostructures. Our method is directly applicable to ten-million-atom nanostructures, such as crystal phase quantum dots. The first steps of strain (only for lattice mismatched systems) and the empirical tight-binding calculation are followed by the efficient calculation of Coulomb matrix elements and the configuration interaction approach. Our approach redefines the tight-binding LCAO single particles wave-functions on a three-dimensional, regular grid. The process of wave-function reconstruction can be performed efficiently by relying of a finite extent of basis orbitals, with the cut-off radius smaller than 2.5 nm. The grid step of about 0.8–1.0 Å was found sufficient for the convergence of the key Coulomb and exchange integrals affecting excitonic spectra. The grid reproduced form of the wave-function allows for the application of Fourier space methods for the calculation of Coulomb matrix elements that benefit tremendously from the Fast Fourier Transform algorithm. Our method goes beyond traditional two-center and monopole-monopole approximations, further our approach can account for different models of dielectric screening function and utilize different basis set such as those generated by TB-DFT approach or new schemes of tight-binding parameterization. We studied the role of a basis by comparing results obtained with Slater-type and Herman-Skillman orbitals and the simplified \( O(N^2) \) approach. We analyzed the effects of basis locality and orthogonality and found that long-range tails of basis orbitals affect significantly values of important electron-hole exchange integrals. The effect of local basis orthogonality is particularly important for calculations involving bright- and dark- excitons splitting. The straightforward application of highly non-orthogonal Slater-type orbitals would lead to severe overestimation of bright-exciton splitting as compared with other approaches. On the other hand Herman-Skillman orbitals, or recently optimized Slater-type orbitals, should correspond more closely to the actual atomic states, however more accurate calculations of the excitonic fine structure should involve basis sets directly designed for tight-binding calculations.

Finally, we illustrate our approach with the calculation for the crystal phase quantum dots with diameter exceeding 70 nm and number of atoms exceeding 10 million. We demonstrated pronounced diameter dependence of both the effective gap and the excitonic binding energy, with transition to nearly bulk-like binding energy for the largest diameter system.
Linear scaling with number of atoms opens a route for semi-empirical atomistic calculations of large semiconductor systems with number of atoms reaching $10^8$ in near future. Due to its efficiency, the method should allow for new possible application such as self-consistent calculations for multi-million-atom nanosystems or accurate nanostate excitonic calculations involving large many-body basis sets. The range of potential applications varies from quantum dots of different species, through nanowires, up to modeling of electronic properties of single dopants embedded in multi-million-atoms transistors.

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