Perturbative approximations to avoid matrix diagonalization

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Abstract

With the aim of developing linear-scaling methods, we discuss perturbative approaches designed to avoid diagonalization of large matrices. Approximate molecular orbitals can be corrected by perturbation theory, in course of which the Laplace transformation technique proposed originally by Almløf facilitates linear scaling. The first order density matrix P corresponding to a one-electron problem can be obtained from an iterative formula which preserves the trace and the idempotency of P so that no purification procedures are needed. For systems where P is sparse, the procedure leads to a linear scaling method. The algorithm is useful in course of geometry optimization or self-consistent procedures, since matrix P of the previous step can be used to initialize the density matrix iteration at the next step. Electron correlation methods based on the Hartree-Fock density matrix, without making reference to molecular orbitals are commented on.

Keywords: linear scaling, density matrix, Laplace-transform, idempotency conserving iteration

1. INTRODUCTION

Computational effort required by diagonalization of matrices scales cubicly with the matrix dimension. In quantum chemistry, one often meets problems for which the dimension is so large that explicit diagonalization, even with the aid of modern computers, is prohibitive. In electron correlation calculations, if configuration interaction (CI) is used, the dimension of the Hamiltonian matrix shows a factorial dependence on the system size (number of electrons/basis functions). This area was therefore the first where Lanczos-type iterative methods were applied, where one or more eigenvectors of the matrix are sought by acting with the matrix on a trial vector repeatedly. A disadvantage is that it may be difficult to obtain eigenvectors more than a few. Quantum chemical applications to the CI problem became revolutionized when the action of the Hamiltonian on the trial vector was directly formulated, so that the huge Hamiltonian matrix was never explicitly constructed ("direct CI" see ref.[1]), and when the iterative procedure was accelerated by diagonalizing the small matrices of the Hamiltonian in the iterative subspace (Davidson's technique[2].

In standard one-electron theories the diagonalization of a one-electron Hamiltonian (Fockian, Kohn-Sham matrix or a simple Hückel Hamiltonian) is required. Albeit these have much smaller size as compared to CI matrices (their dimension being simply the basis set size), large molecular systems or nanostructures may induce serious computational difficulties making it necessary to avoid explicit matrix diagonalization.

In this paper, we shall review two approximation approaches which avoid the explicit diagonalization of large one-electron Hamiltonians. The Hamiltonian may either be a one-electron operator by construction (Hückel, tight-binding) or may emerge from theories that start with the many-electron Hamiltonian and arrive to an effective one-electron operator (Hartree-Fock, Kohn-Sham) via appropriate approximation steps. The formulae we are going to discuss are applicable in both cases.

The literature of density matrix calculation without making reference to molecular orbitals is huge. We mention Green-function techniques[3, 4], numerical minimization procedures[5–9], divide and conquer algorithms[10–12], renormalization group techniques[13, 14], using the sign matrix of the Hamiltonian[15]. Reviews Refs.[16, 17] may also be consulted for getting an orientation in the field. Here, we do not aim to review all the above methods. Rather, we detail two perturbative schemes developed in our laboratory, discussing only the closely related approaches. We shall also elaborate procedures that step beyond the one-electron model and aim the calculation of electron correlation based on the density matrix obtained at the one-electron level.

2. PERTURBATIVE ENERGY ESTIMATION USING LAPLACE TRANSFORM

Let us assume that we have a large molecular system, defined over a basis set of atomic orbitals (AOs) $\{\chi_\mu\}$, and an *approximate* set of molecular orbitals (MOs) $\{\phi_i\}$. On approximate MOs we mean a set of occupied and virtual orbitals selected by chemical intuition, which do not exactly obey the Brillouin theorem. An example is, for a system of two or more interacting nanosystems, the ensemble of the MOs of the isolated subsystems. If the interaction is not too strong, it can be conveniently handled by perturbation theory (PT), leading to the second order formula

$$E^{(2)} \;=\; -\sum_{i}^{occ}\sum_{k}^{virt} \frac{W_{ik}W_{ki}}{\varepsilon_k - \varepsilon_i}, \tag{1}$$

with i, k being MO indices and ε are the respective zero-order one-particle energies. If the number of MOs is very large, computation of the above formula, especially evaluation of the effective matrix elements W_{ik}, is time consuming. The main difficulty is that matrix W in the approximate one-particle MO set is usually not sparse. Expanding the MOs φ as linear combinations of AOs χ:

$$\varphi_i \;=\; \sum_{\mu} iC^m u\; \chi_\mu, \tag{2}$$

one might attempt to transform Eq.(1) to the original basis of site-centered AOs. However, substituting (2) into (1) alone is not useful from the computational point of view, since the energy denominator prevents one to perform the summation over MO indices k and i independently.

An ingenious idea for factorizing the energy denominator in PT was proposed by Almlöf [18, 19], who applied the identity

$$\frac{1}{\varepsilon_k - \varepsilon_i} \;=\; \int\limits_0^\infty e^{-s\varepsilon_k} e^{s\varepsilon_i}\; ds, \tag{3}$$

which is the formula for the inverse Laplace transformation of $(1/x)$, with x standing for the energy denominator. The integral is convergent if the energy gap between the occupied and virtual states, $\varepsilon_k - \varepsilon_i$, is positive. This idea has been applied to the evaluation of electron correlation energy with considerable success[19–21].

Substituting identity (3) into (1) and using that $W_{ik} = \langle\varphi_i|W|\varphi_k\rangle$, we get the expression

$$E^{(2)} = \int\limits_0^\infty e(s)\, ds \tag{4}$$

with

$$e(s) = \sum_{\mu\nu\lambda\sigma} t_{\mu\nu}\, f^p_{\nu\lambda}(s)\, t_{\lambda\sigma}\, f^h_{\sigma\mu}(s), \tag{5}$$

where $t_{\mu\nu} = \langle\chi_\mu|W|\chi_\nu\rangle$ is the effective hopping interaction between localized sites, and we have introduced the notations for the s-dependent energy-weighted density matrices

$$\begin{aligned} f^p_{\nu\lambda}(s) &= \sum_k^{virt} e^{-s\varepsilon_k}\, C^k_\nu C^k_\lambda \\ f^h_{\sigma\mu}(s) &= \sum_i^{occ} e^{\,s\varepsilon_i}\, C^i_\mu C^i_\sigma. \end{aligned} \tag{6}$$

Since matrix t, in contrast to W, is extremely sparse in several applications, a very fast evaluation of Eq.(5) is possible at the price of a quadrature (4). This obviously facilitates an $\mathcal{O}(n)$ treatment for large systems if the number of nonzero t and f matrix elements grows linearly with the system size.

As an illustration of the sparseness, we present elements of the Hückel density matrix of carbon nanotubes in Fig. 1 as a function of the distance between sites μ and ν. Apparently there is an exponential decay in the case of a semiconducting tube (note the logarithmic scale). Obviously, the same behaviour is inherited by energy weighted density matrices $f^p(s)$ and $f^h(s)$. For these systems calculation of the interaction energy may bring a considerable time gain if exploiting sparsity when multiplying matrices according to Eq.(5). Gap-less systems, like the case of a metallic tube shown if Fig. 1 show a different behaviour. For these systems density matrix elements hardly decay with the distance, hence matrix multiplication in Eq.(5) remains formally proportional to N^3.

The appealing feature of Eq.(5) is that only the site-site interaction matrix t depends on the relative position of the interacting partners, while the energy-weighted density matrices are solely characteristic to the zero-order (noninteracting) subsystems. These, therefore, should be evaluated just once when scanning the interaction energy surface. In addition, if the subsystems happen to be identical (cf. a molecular crystal), one can make use of the fact that their matrices f^p and f^h are the same. All of this may result in orders-of-magnitudes saving in computational time, if the second order energy $E^{(2)}$ is to be evaluated at many points in configuration space, provided that the structure of interacting partners is kept rigid.

We illustrate this idea on the example of interacting carbon nanoclusters treated at the Hückel-level. Each carbon atom is considered as a site, and an effective one-electron-per-site model is used with the Hamiltonian

$$\hat{H} \;=\; \sum_{A} \hat{H}^A \;+\; \sum_{A<B} \sum_{\mu \in A} \sum_{\nu \in B} t_{\mu\nu} \;(a^\dagger_\mu a_\nu + \mathrm{h.c.}). \tag{7}$$

Here A runs over the subsystems (in Table I e.g. A=1 is the C_{60} molecule, A=2 is the (10,10) nanotube), $\hat{H}^A$ is the Hamiltonian of the isolated subsystem A, while $t_{\mu\nu}$ are the inter-system hopping matrix elements for which we take $t_{\mu\nu} = -t^0 S_{\mu\nu}$ with the overlap integral $S_{\mu\nu}$ between Slater type carbon $2p_z$ orbitals with an exponent of ζ=2.895 Å^{-1} oriented normally to the molecular surface. (Intermolecular Hückel Model, IMH)[22]. The spirit of the model is the similar to that of Stafström's [23–25]. Similar models were also applied recently to DWNTs [26, 27].

Solution of the model involves the following steps: (i) the *in vacuo* Hamiltonians H^A are diagonalized separately for both monomers and the energy-weighted density matrices f^h and f^p of Eq.(6) are saved; (ii) the inter-system hopping interaction is computed in second order via (4) and (5); (iii) to describe non-hopping effects, a van der Waals type 6-12 site-site potential is added to the interaction energy with A_6=25.667 eV and A_{12}=154447.9 eV. (The above values of parameters t_0, ζ, A_6 and A_{12} were obtained by fitting to results of ab initio calculations on small systems.)

The time requirement for calculating the interaction energy of a pair of aligned pieces of semiconducting carbon nanotubes is presented in Fig. 2. For about 1500 sites the calculation time of second order PT are similar by ordinary means – Eq.(1) – and by the Laplace transformed expression – Eq.(4). However Eq.(1) shows a more drastic increase in computation time with system enlargement if compared with the application of Laplace-transformed denominators in Eq.(4).

Formula (4) has been applied successfully for the exploration of interaction energy surfaces of weakly interacting nanoclusters like bundles of tubes[28] and double wall nanotubes[29]. Here we present the characteristics of the interaction energy hypersurface of a fullerene molecule encapsulated within a (10,10) nanotube. Relative position of the fullerene and the tube was varied by fixing the tube and pulling and rotating the C_{60} molecule till a grid of all non-equivalent geometry points were produced. A 2 dimensional cross-section of the interaction surface is plotted in Fig 3 for illustration. Here the energy is given as a function of the position of the fullerene and the angle of its rotation around the tube axis. To characterize the hypersurface in numerical terms, energy minima and maxima are collected in Table I for three specific orientations of the C_{60} molecule, i.e. when it shows either a 6-membered ring, a 5-membered ring or an apex atom towards the tube end. Based on Fig. 3 and Table I we may state that the energetic barriers to overcome when dragging a fullerene molecule encapsulated in a nanotube along the tube axis range from a few hundredth to a few tenth of an electronvolt. If following the minimum energy path, the molecule would rotate when advancing in the tube.

In concluding, factorization of energy denominators of second order perturbation theory in combination with the application of effective Hamiltonians may result in several orders of magnitude saving of computational work. The key idea is that if one describes the interaction between two or more subsystems with an effective Hamiltonian at many points in the configuration space, the most demanding part of the computations (namely, the construction of the energy weighted density matrices (6)) should be performed only once. The condition under which this drastic simplification is possible is that the interaction should be small enough to justify a perturbative treatment with *rigid* monomers. This also involves that the effective Hamiltonian should be constructed in a way that any overlap between monomers is neglected at the zero order. Since these conditions are quite general, we hope that the idea will induce widespread applications in many areas.

3. ITERATIVE SEARCH FOR THE DENSITY MATRIX

Several procedures have been proposed which attempt to find the one-electron density matrix (P) directly, instead of constructing it from the occupied eigenvectors. A direct search of the density matrix, has to take care of the N-representability conditions[30], which are, at the one-electron level, the hermiticity, the idempotency and the correct trace of P. While hermiticity and $\mathrm{Tr}(P) = N$ can usually easily be ensured, idempotency is often violated. To restore idempotency P is usually subjected to purification algorithms[6, 9, 31–33].

We review below a simple iterative formula for P, having the essential feature of idempotency conservation. That is, if one starts with an idempotent initial guess, the idempotency of P is exactly preserved during the iteration so that no purification is needed. The trace of the initial density matrix is also conserved. At convergence, matrix P is fully N-representable and provides the exact energy corresponding to one of the exact wave functions of the model Hamiltonian.

Consider an effective one-electron Hamiltonian matrix H, which is the Hückel Hamiltonian in a noninteracting model or the Fockian in a self-consistent procedure. The exact density P, as represented in an orthogonal basis satisfies the equation[6]

$$[H, P] = 0,$$

which, upon multiplying by P from the right, can be recast to a Bloch-type equation

$$HP - PHP = 0$$

or

$$QHP = 0$$

where $Q = 1 - P$ is the hole density matrix. This equation is essentially equivalent to the Brillouin theorem, and can also be derived from the contracted Schrödinger equation[34]. The latter equation suggests the iterative formula

$$P^{'} = P + \eta \ (QHP) \tag{8}$$

where η is an arbitrary parameter a proper value of which can be selected to facilitate the convergence of the iteration.

It is easy to see that, at any values for η, both the idempotency ($P^2 = P$) and the correct trace ($\mathrm{Tr}\ P = N$) conditions are preserved upon iterating Eq.(8). As to the former property:

$$(P^{'})^2 = P^2 + \eta PQHP + \eta QHPP + \eta^2 QHPQHP = P + \eta QHP = P^{'}$$

where we have used that $P^2 = P$ and $PQ = 0$. The trace is conserved since

$$\mathrm{Tr}\ P^{'} = \mathrm{Tr}\ P + \eta \mathrm{Tr}\ QHP = \mathrm{Tr}\ P.$$

The latter equation holds as $\mathrm{Tr}\ QHP = \mathrm{Tr}\ PQH = 0$.

Apart from idempotency and correct trace, P has to fulfill one further requirement: it has to be self adjoint. Based on this, one can prove that Eq. (8) cannot converge to the exact density matrix. The proof is as follows. Assume that starting from an approximate, hermitian one-matrix P_0 and the associated hole-matrix Q_0, we have arrived at the exact matrix P by iterating Eq. (8). One may realize, that every new term appearing in course of this iteration bears a leftmost Q_0 and a rightmost P_0. Thus the exact one-matrix can be written as

$$P \; = \; P_0 + Q_0 h_{\text{eff}} P_0 \tag{9}$$

where an effective Hamiltonian h_{eff} is introduced. Now let us multiply Eq. (9) by P_0 first from the left, then from the right, to obtain $P_0P = P_0$ and $PP_0 = P$. Taking the adjoint of this latter equation and utilizing hermiticity of both P and P_0, we get $P_0P = P$ which, together with the first of the above two equations involves that $P = P_0$. Therefore, for an approximate, hermitian P_0 we have a contradiction.

The source of the contradiction is clearly that $P^{'}$, as defined by Eq. (8), is not hermitian and this property is conserved upon iteration. One may correct for this, realizing that the iteration formula

$$P^{'} = P + \eta \; (PHQ)$$

has also the same trace- and idempotency conserving properties as Eq. (8). It, therefore, facilitates the following double-iteration sequence:

$$\begin{aligned} P^{'} \; &= \; P + \eta \; (QHP) \\ P^{''} \; &= \; P^{'} + \eta \; (P^{'}HQ^{'}) \end{aligned} \tag{10}$$

with $Q^{'} = 1 - P^{'}$. The above two steps can be combined into one to yield

$$P^{''} \; = \; P + \eta \; QHP + \eta \; (P + \eta QHP)H(Q - \eta QHP). \tag{11}$$

Since both steps of Eq.(10) conserve the trace and the idempotency, $P^{''}$ has the correct properties, just like $P^{'}$. Moreover, upon convergence, conditions $QHP = 0$ and $PHQ = 0$ are satisfied to a given accuracy, which involves that matrix P commutes with H. From this, hermiticity of the converged matrix P automatically follows.

Simple perturbational arguments indicate that hermiticity violation diminishes upon iteration by Eq.(11). If one writes $H = h^{(0)} + V$ where V is small, and one starts the iteration with some $P^{(0)}$ which is exact with respect to $h^{(0)}$, one can order the terms coming from the iteration in increasing powers of V. Expanding (11) we can write

$$\begin{aligned} P'' = P^{(0)} \; &+ \; \eta \; \left[Q^{(0)} V P^{(0)} + P^{(0)} V Q^{(0)} \right] \\ &+ \; \eta^2 \; \left[Q^{(0)} V P^{(0)} V Q^{(0)} - P^{(0)} V Q^{(0)} V P^{(0)} \right] \\ &- \; \eta^3 \; \left[Q^{(0)} V P^{(0)} V Q^{(0)} V P^{(0)} \right] . \end{aligned}$$

Assuming that the initial density matrix $P^{(0)}$ is hermitian, the two terms in the first square bracket are adjoints of each other, while the two terms proportional to η^2 are themselves hermitian. The only violation of hermiticity may come from the last term, which is of order 3, and expected to be very small. Further iteration shifts the violation of hermiticity to higher orders, indicating that non-hermitian terms are gradually eliminated during iteration.

Mazziotti applied an alternative way of correcting for the hermiticity violation of Eq.(8): he took the hermitian part of QHP[34]. This way however the idempotency-conserving feature of Eqs.(8) or (10) is lost and one has to apply a purification procedure at each iteration step.

We tested Eq.(10) against a similar, iterative algorithm used by Németh and Scuseria [15] which aims to get the sign matrix of the Fockian. Though the latter often converges much faster, Eq.(10) was found to work better for low-gap systems and metals. In addition, Eq.(10) has the advantage over sign matrix iterations that (i) it does not need an a priori estimation of the chemical potential; (ii) its intermediate results, being idempotent and having the correct trace, give physically meaningful approximations; (iii) iterations can be started from any good guess, e.g. from the P matrix of a previous SCF cycle or, in course of a geometry optimization procedure, from the converged P matrix of a nearby geometry point.

Numerical experience shows that in SCF or geometry optimization procedures, the sign-matrix iteration is better used at the beginning, while as the density matrix P gets converged, its refinement is more advantageous by Eq.(10).

The proper choice of parameter η is crucial[35]: chaotic behavior of the iteration scheme can be expected for a wrongly selected value, since the mapping shown by Eq.(8) is closely related to the logistic mapping which is a prototype for chaotic solutions[36]. The sign of η

can be determined from the condition that the energy should decrease. Looking at the first equation in (10), we can write $E' = E + \eta Tr(QHPH)$, which tells that the energy change is proportional to η. Thus the appropriate sign of η can always arrange the energy to decrease in an elementary step. This, if the initial P is properly chosen, will ensure that we converge to the ground state.

In Refs.[37, 38] illustrative applications were presented at the Hückel level as well as for Hartree-Fock calculations. To determine the magnitude of η, the following strategy was applied. For a physically related small system the best η was found by numerical experience. As we observed a great universality in the value η when changing the system size, the same value could be used effectively for the calculation of the larger system. Using sparse matrix technology, one may easily perform each individual iteration in a linear scaling manner. we applied a ”flexible” technology, storing only the nonzero elements of all matrices along with two linear arrays for row and column indices. Standard matrix manipulation routines for this technology are available [39]. The effectiveness of this approach clearly depends on the extent of sparsity of the matrices.

In summarizing, we proposed a new iterative solution of the Bloch-type equation for the first order density matrix of a one-electron model. If the number of electrons is known, no prior knowledge of the chemical potential is required, and no purification transformations are needed since the iteration preserves both the trace and the idempotency properties of the one-matrix.

4. ELECTRON CORRELATION

4.1. E2[P] functional

Having obtained the density matrix by a linear-scaling procedure directly we do not have a set of molecular orbitals (MOs) in our possession. Standard methods of electron correlation like usual second order Møller-Plesset (MP2) or coupled clusters singles doubles rely on a set of occupied and virtual MOs, hence they are not directly applicable. However, there exists schemes that provide correlation energy merely from the P matrix.

The origin of such an approach may be the observation that the MP2 energy is a functional of the Hartree-Fock density matrix [40]. This functional can be explicitly constructed by the Laplace-transformed version of the MP2 energy formula. Resolving the MP2 energy in a way analogous to Eq.(4), the s-dependent energy can be given as[40]

$$e^{[2]}(s) = \tag{12}$$
$$-\frac{1}{2}\sum_{\mu\nu\lambda\sigma}\;\sum_{\rho\tau\eta\kappa} X_{\mu\rho}(s)Y_{\nu\tau}(s)X_{\lambda\eta}(s)Y_{\sigma\kappa}(s)\;\;(\rho\tau|\eta\kappa)\;\;[(\mu\nu|\lambda\sigma)-(\mu\sigma|\lambda\nu)]$$

in terms of atomic spin orbitals. In this equation $X(s)$ and $Y(s)$ are energy-weighted particle and hole density matrices (EWDMs) defined by matrix P as

$$X(s) \;=\; e^{sPF}\;P. \tag{13}$$

and

$$Y(s) \;=\; e^{-sQF}\;Q. \tag{14}$$

where $Q = S^{-1} - P$ is the hole density matrix.

If both matrices F and P are sparse, the exponential of their product can be clearly obtained through the Taylor expansion in a linear scaling manner. The expansion is expected to be rapidly convergent for small s, while for large s values one may obtain matrices X, Y by using

$$e^{jsPF} = \left[e^{sPF}\right]^j$$

for integer j, which limits merely the choice of quadrature points in course of the numerical integration over s.

It is interesting to note that not only the MP2 energy can be considered as a functional of the HF density matrix. In fact, applying a double resolution, the third order energy is recast as

$$E^{[3]} = \int_0^\infty\int_0^\infty e^{[3]}(s,s')ds\;ds', \tag{15}$$

while the evaluation of the MP4 formula would require a triple integration

$$E^{[4]} = \int_0^\infty\int_0^\infty\int_0^\infty e^{[4]}(s,s',s'')ds\;ds'ds'' \tag{16}$$

with an obvious increase of numerical difficulty throughout the quadrature. Numerical realization of the procedure at order two was performed by Nakai et al.[41, 42].

4.2. The FLMO approach

Even if the full density matrix is not constructed from a set of MOs, there are several ways to construct orbitals based on matrix P. In the frozen localized molecular orbital (FLMO) approach[43], one obtains localized MOs by projecting atomic orbitals $|\chi\rangle$ into the occupied space:

$$|\varphi_i^{\mathrm{occ}}\rangle = \sum_\mu (PS)_{\mu i} \, |\chi_\mu\rangle.$$

Similarly, virtuals emerge by projecting AOs with matrix QS. In the FLMO philosophy, AOs of an active site of a large molecule are used for projection, thus the resulting MOs will be, to a great extent, localized on that site. These active LMOs may be used to compute the correlation energy of the fragment. LMOs falling out of the active site are never explicitly constructed, the serve as a frozen core for the active part of the correlation energy.

In concluding, we have mentioned two alternatives of calculating electron correlation based on the Hartree-Fock P matrix. One may either express the desired correlation energy formula in terms of the density matrix, or utilize P to define a set of molecular orbitals. By the latter approach the number of orbitals, and consequently the calculation time of the correlation energy can be kept under control. Moreover the orbitals are localized on a preselected region of the molecule. These features represent an advantageous starting point for future developments towards efficient calculation of local correlation energies.

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Figure legends

Fig. 1 Elements of the density matrix obtained at the Hückel level, for finite size carbon nanotubes. A (11,9) tube is taken as a prototype for a "semiconducting tube", a (10,10) tube was computed to illustrate a "metallic tube".

Fig. 2 Calculation time spent on computing the interaction energy by the intermolecular Hückel model for aligned pairs of finite size carbon nanotubes.

Fig. 3 Interaction energy of a C_{60} molecule and a piece of a (10,10) nanotube, as a function of the relative orientation of the interacting partners. The fullerene is encapsulated within the tube. Position of C_{60} within the tube is measured on axis x, rotation angle of C_{60} around the tube axis is varied on axis y. The nanotube is kept fixed.

Table caption

Table I Maxima and minima on the interaction energy surface of a C_{60} molecule advancing and rotating within a piece of a (10,10) carbon nanotube. The face of the C_{60} as seen looking from the tube end is indicated as table heading. Rotation of C_{60} is performed around the C_{10} axis of the nanotube. Axes x and y span 2.5 Å and 72 ^{o} respectively while the vertical axis z spans 0.28 eV.

TABLE I:

	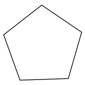	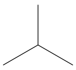	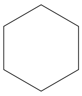
maxima [eV]	-9.05	-9.12	-9.12
minima [eV]	-9.33	-9.23	-9.17
largest barrier [eV]	0.28	0.12	0.05

FIG. 1:

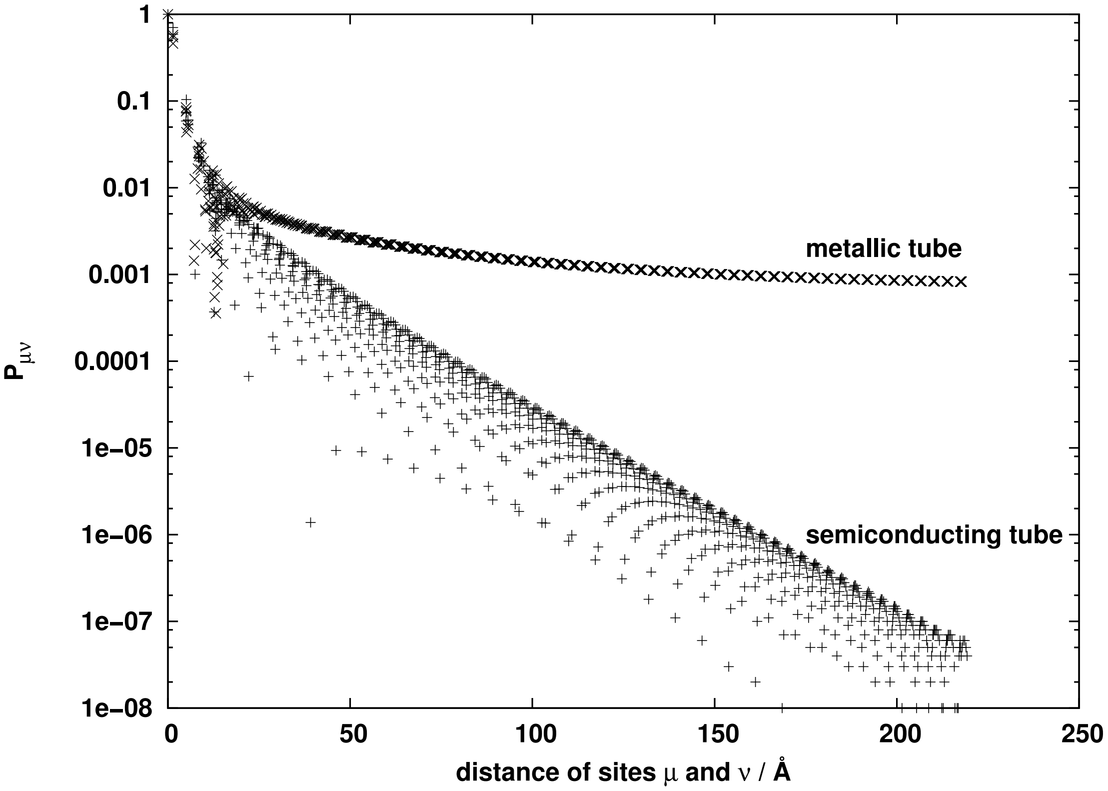
1
0.1
0.01
0.001
0.0001
1e-05
1e-06
1e-07
1e-08
$P_{\mu\nu}$
0
50
100
150
200
250
distance of sites μ and ν / Å
metallic tube
semiconducting tube

FIG. 2:

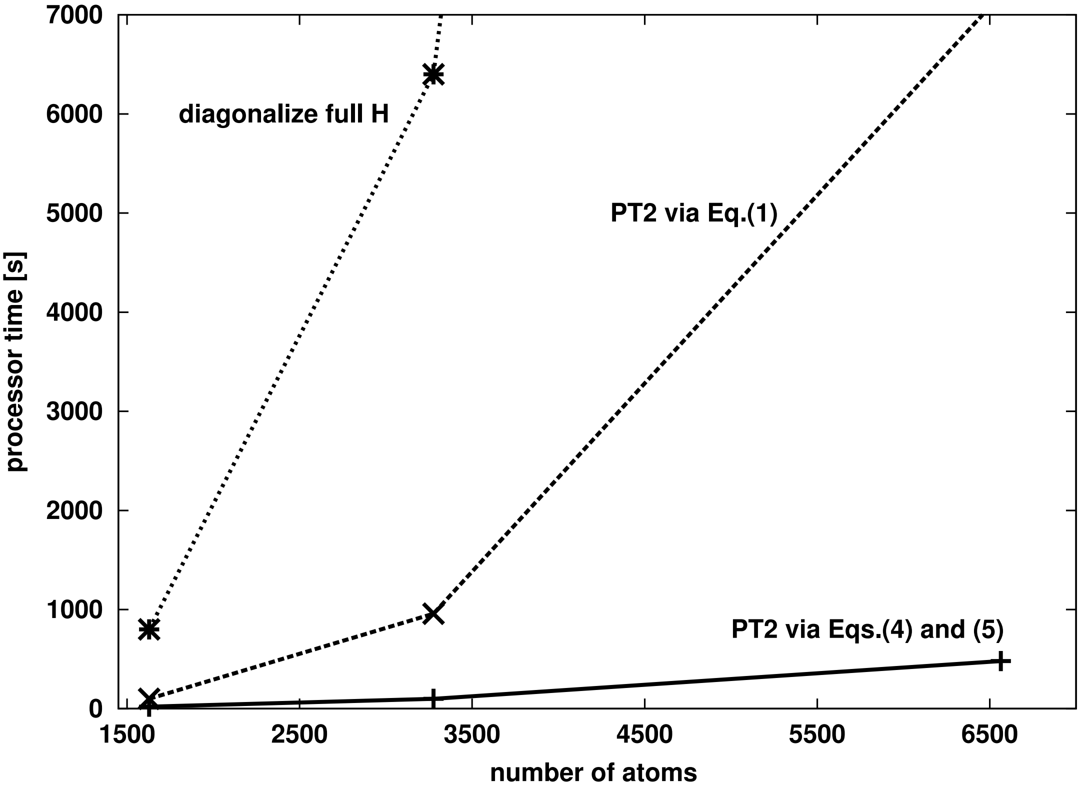
7000
6000
5000
4000
3000
2000
1000
0
processor time [s]
1500
2500
3500
4500
5500
6500
number of atoms
diagonalize full H
PT2 via Eq.(1)
PT2 via Eqs.(4) and (5)

FIG. 3: