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A new approach to dynamical determination of the active zone in the framework of the hybrid model (quantum mechanics/ molecular mechanics)

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Abstract

A new approach to dynamical determination of the active zone in the framework of the hybrid model (quantum mechanics/ molecular mechanics) is developed in this work. The proposed approach is based on using of the original method for calculation of the local stress on the atoms of structure, experiencing different external influence. The algorithm of realization of the proposed approach in the framework of the hybrid model ‘hot spot’ using the quantum tight binding method and empirical method based on REBO potential is described in details. The test problem of simulation for behavior of zigzag carbon nanotube at the tension is solved to approbate the presented approach.

Keywords: hybrid method (QM/MM); hot spots; local stress; tight binding method; REBO potential

1. Introduction

At the present time, the computer simulation is one of the main tools to identify the regularities of behavior of the molecular systems under various external influences. The carrying out of high-precision numerical experiment allows us to predict the properties of the molecular objects and to create the models of the functional devices based on them. The following classes of the computer simulation method of the molecular nanosystems are widely known:

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ab initio methods Roothaan, C. C. J. (1960); Jensen, F. (2007); Cramer, Christopher J. (2002), the methods based on the density functional theory Kohn, W., Sham, L. J. (1965); March, N. H. (1992), semi-empirical Michael J. S. Dewar and Walter Thiel (1977); James J. P. Stewart (2007) and empirical methods Tersoff J. (1989); Brenner D.W. (1990). These methods have several advantages, however, are not without disadvantages. In particular, the most accurate ab initio methods have enormous computational complexity, so one can apply their only to study the low-atomic objects. Empirical methods allow us to consider a system, consisting of a large number of the atoms, but the methods of this class do not consider many qualitative features of the molecular systems. At the same time sharing of the methods of different classes allows us to achieve the optimal accuracy of the calculations and investigate the system of large dimension. A new class of methods, combining the molecular and quantum mechanical model Kerdcharoen T. et al., (1996); Kerdcharoen T. et al. (2003), can serve this problem. This class of methods was called as hybrid molecular dynamics methods (QM/MM). This class will realize methods of the numerical experiment with multiatomic structures in real time with external conditions: fixed and variable electric fields, thermal effects, constant and changing mechanical load, plasma, adsorbed atoms. Application of this method allows us to increase the speed and accuracy of calculations.

The majority of the hybrid methods based on fragmentation of the investigated systems on three local zones (active, the buffer zone and the surrounding zone). The active zone is entirely modeled using the method of high accuracy, for example QM method, surrounding zone is modeled using the method of less precise, such as MM method. The transition from one method to another is occurs in the buffer zone. In the framework of the ‘hot spot’ Kerdcharoen T. et al., (1996) method so-called hot spots are extracted in the molecular structure. They may, for example, small molecules entering in some homogeneous environment and reacts with that environment. Then the environment is calculated using molecular mechanical method except a some neighborhood of the hot spot area. It is also possible to highlight hot spots around defects on the surface of nanostructures, or in the areas subject to severe stress. In the framework of the current method all atoms, entering in the active zone the sphere of some radius relative on hot spot, is calculated using the linear combination of quantum and molecular-mechanical method. All atoms, not entering in the sphere of radius rout, are calculated using the molecular mechanics method (pic. 1). The total energy of molecular system is determined according to formula

\[ E = E^{entire}(MM) + (E^{A+B}(QC) - E^{A+B}(MM)), \]

where \( E^{entire}(MM) \) — the total energy of system, are calculated using molecular mechanics method. \( E^{A+B}(QM) \) — the energy of molecular system consisted of atoms, entering in the active and buffer zone, are calculated using quantum chemical method. The zero level of energy is chosen so that the energy of molecular system in the ground state for both methods was equal to zero. It is possible solve the statistics problems using current potential by minimization of potential \( E \).

To calculate using molecular dynamics it is necessary to determine the forces, acting on each atom. The calculation of forces, acting on each atom, is carried out according to formula

\[ f_i = f_i^{entire}(MM) + S(r_i)(f_i^{A+B}(QC) - f_i^{A+B}(MM)). \]

Where \( r_i \) the distance from the \( i \)-th atom to the center of the active zone, \( S (r) \) — the scaling function
The unsolved problem of correct from a physical point of view justify of location of the active zone and the dynamics of its changes over time remains at using of the hybrid methods to model the behavior of the molecular systems. This work is devoted to the development of the algorithm for determining of the active zone boundaries, based on the using of the original methods for calculation of the local stress on the atoms, experiencing external influence.

2. The method for calculation of the local stress of atoms

We proposed an original method to calculate the stress near the atom. The following idea is based on the aforementioned method. The stress on all the atoms of a nanostructure, being in a ground (equilibrium) state, is supposed to be equal to zero independently on where the atom is located (at the boundary or in the middle of the structure). Such situation corresponds to the unloaded free state of the nanostructure. Along with it, each atom possesses self-energy which is determined by its nature and its environment. It is assumed that the stress is non-zero if the external factors act on the atomic grid: external deformed force, adsorbed atoms, eliminated atoms, etc. Since, owing to the external influence, the distribution of the energy among the atoms alters, then the value of the difference between the energy of the atom in the deformed grid and that on an unloaded (free) grid would reflect the degree of deformation in the considered point of the structure, notably the atomic grid stress near the current atom. We would consider this value as a stress Glukhova O.E. et al. (2013).

It is proposed to carry out the calculation of the local stress field according to the followed algorithm.

1. Optimization of the initial structure by means of the quantum-chemical method.
2. Calculation of distribution of the bulk energy density per atom using the empirical method.
3. Search of the atomic configuration of the nanostructure subjected to the external influence as a result of the energy minimization for coordinates, using the quantum-chemical method.
4. Calculation of the distribution of the bulk energy density per atom in the structure subjected to the external influence, using the empirical method.
5. Calculation of the local stress in the atomic grid according to the difference between the values of the bulk density of energy for the atoms of the structure subjected to the external influence, and the initial structure.

Optimization of the structure after and before the deformation was carried out by means of the tight-binding method. The optimization was performed by minimizing the total energy for the coordinates of all the atoms. Calculation of distribution of the bulk energy density amongst the atoms was performed by the empirical method. This method is based on the Brenner’s potential Brenner D. W. (1990) with the introduced torsion interaction energy and van der Waals interaction energy Stuarta S.J. (2000). The bulk energy density of the atom i was calculated by the formula:

\[
\omega_i = \sum_{j \neq i} \left( V_p(r_{ij}) - B_{ij} V_A(r_{ij}) \right) + \sum_{j \neq i} \sum_{k \neq i} \sum_{l \neq i} V_{\text{tors}}(w_{ijkl}) + \sum_{j \neq i} V_{\text{vvdw}}(r_{ij}) \right) / V_i, \tag{4}
\]

where \( V_p(r_{ij}) \) and \( V_A(r_{ij}) \) are the pair of potentials of repulsion and attraction between chemically bonded atoms, which is determined by the atoms type and the distance between them. \( r_{ij} \) is the distance between atoms \( i \) and \( j \), \( i \) and \( j \) are the numbers of interacting atoms; \( B_{ij} \) is the multiparticle term correcting interaction energy of the atoms pair \( i, j \) (considering specificity of interaction of \( \sigma - \) and \( \pi - \)electron clouds); \( V_{\text{tors}} \) is the torsional potential, which is the function of the dihedral angle constructed on the basis of atoms with an edge on bond \( i; j \) (\( k \); \( l \) are the atoms...
forming chemical bonds with \(i; j\). \(V_{\text{vdW}}\) is the van der Waals interaction potential between chemically unbonded atoms; \(V_{i} = 4/3 \pi r_{0}^{3}\) is the occupancy volume of the atom \(i\), \(r_{0}\) is the Van der Waals radius of the carbon atoms which equals to 1.7 Å.

The stress of the atomic grid near the atom with number is calculated as:

\[
\sigma_{i} = \left| w_{i} - w_{i}^{0} \right|,
\]

where \(w_{i}^{0}\) is the bulk energy density of \(i\)-th atom of the graphene sheet which is in equilibrium; \(w_{i}\) is the bulk energy density of an atom of the graphene sheet subjected to the external influence (deformation, defects formation, and etc.). The value of in the centre of the graphene sheet is equal to -58.60 GPa. At the edges of the graphene sheet the bulk energy density is higher since the atoms of the edges have only two links with other carbon atoms. It is equal to -41.54 GPa on armchair edge and on zigzag edge is equal to -40.64 GPa. It is suggested that the stress equals to zero for the atoms in the center and at the edges.

![Fig. 2. The combining of the active and buffer zones. The boundaries of the active zone are marked in red, the boundaries of the buffer zone — in blue.](image)

The proposed method for calculation of the local stress near atom was successfully applied at the investigation of the graphene nanoribbon with a defect induced by hydrogenation of one hexagon Glukhova O.E. et al. (2012). Also, the current method was used for estimation of the tensile strength for graphene sheet at the nanoindentation by the platinum pyramid Glukhova O.E. et al. (2012). It was shown that the C-C bonds are breaking in the fields, where the stress on the atoms was maximum. These value was equal to ~42 GPa are critical for the considered structure.

In this work we proposed to use the original developed method for calculation of the local stress to reveal the active and buffer zones in the framework of the hybrid method QM/MM. Namely, we will considered that all atoms, having the critical stress, and their nearly environment get in the active zoned (atoms, entering in the sphere of the radius \(r_{\text{out}}\)).

At the deformation, in the general case, the atoms, experiencing the critical load, can be located in different zones, forming thereby some hot spots. If two or more active or buffer zones cross, they must be combined into a single (see Fig. 2). In this case the combined active zone will be contains all atoms, entering at least into one of these active regions. Relevant buffer zone will be formed from all the atoms that entering into at least into one of the buffer areas and do not enter into either the active region. Such combined active zones were called as hot region. To determine the hot region one can use the algorithm for selection of the strong connectivity components on a graph, for example, the Tarjan’s algorithm Tarjan R.E. (1972).

3. Details of realization of the hybrid method QM/MM

The proposed approach was realized in the framework of the ‘hot spot’ method using tight binding method as a method of higher-order accuracy and method based on REBO potential as a method of lower order accuracy.
The finding of the forces, acting on the atoms of the molecular system is a key moment in molecular dynamics simulation algorithm. The calculation of the forces in the framework of the molecular dynamics is a trivial problem. Therefore, let us discuss in detail the calculation of the forces in the framework of the tight binding method.

The potential energy of a system within tight binding method is determined by relation

$$ E_\text{tot} = E_\text{bond} + E_\text{rep}, \quad (6) $$

where $E_\text{bond}$ is the energy of the occupied electronic states including the spin, $E_\text{rep}$ is the repulsive energy, which is a result of the electronic interaction between atoms.

It is known, that in the framework of molecular dynamics the forces are calculated as a gradient of the potential energy of the system. The calculation of the gradient of the energy $E_\text{rep}$ do not presents the large computational complexity. Let us in detail on the calculation of the gradient of the energy $E_\text{bond}$.

The bond structure energy is determined by the formula:

$$ E_\text{bond} = 2 \sum_n \epsilon_n, \quad (7) $$

This expression is the sum of energies of the molecular orbitals obtained by diagonalizing the Hamiltonian. $n$ is the number of the occupied orbitals, and $\epsilon_n$ — the energy of the single-particle orbitals. The overlap matrix elements are calculated by the formulas which take into account four types of interaction: ss; sp; pp; pp:

$$ V_{ij}(r) = V^0_{ij}(\frac{P_i}{r})^p_1 \exp \left( p_1 \left( \frac{R_i}{P_2} \right)^p_2 + \left( \frac{R_j}{P_2} \right)^p_3 \right), \quad (8) $$

where $i$ and $j$ are the orbital moments of wave function, $\alpha$ presents the bond type ($\sigma$ or $\pi$). The atomic terms $\epsilon_s$, $\epsilon_p$ are the atomic orbital energies of carbon which found on the main diagonal of the Hamiltonian. The values of the $\epsilon_s$, $\epsilon_p$ atomic terms, the parameters $p_\alpha$ (n = 1, 2, 3, 4) and the equilibrium overlap integrals $V^0_{ij}$ ($V^0_\text{ss}$, $V^0_\text{sp}$, $V^0_\text{pp}$) are described in details in the work O.E. Glukhova et al., (2006). The coefficients $p_\nu$, $p_\mu$, are the power exponents, the coefficient $p_\sigma$ is determined by the overall shape and steepness of the function, and the parameter $p_2$ is a cutoff distance for the hopping matrix elements.

To obtain gradient of the energy $E_\text{bond}$ we differentiate the formula (7) by $r_i$:

$$ \frac{\partial E_\text{bond}}{\partial r_i} = 2 \sum_n \frac{\partial \epsilon_n}{\partial r_i} \quad (9) $$

To determine $\partial \epsilon_n/\partial r_i$ it is need to establish the relationship between the change in the eigenvalues of the Hamiltonian and change elements of the Hamiltonian.

According to matrix perturbation theory by J. H. Wilkinson, a perturbation of matrix $A$ which dependends on parameter $\delta$ can be represented as

$$ A(\delta) = A + A_1 (\delta), \quad (10) $$

where $A_1$ is some matrix.

Using algebraic approach Wilkinson obtained a representation of perturbed eigenvalues as a convergent series

$$ \lambda_i(\delta) = \lambda_i + k_1^i \delta + k_2^i \delta^2 + \ldots, \quad (11) $$

where $\lambda_i$ are eigenvalues of matrix $A$ and $\lambda_i(\delta)$ are eigenvalues of perturbed matrix $A(\delta)$.

In this expansion coe cients $k_1^i$, $k_2^i$, … are determined by the following correspondence:

$$ k^i_j = \sum_{l=1}^{m} \frac{t^i_{jm} \beta_{ji}}{s_j}, \quad (12) $$

where

$$ t^i_{jm} = \frac{t^i_{jm} (\lambda - \lambda_i)^{j-m-1}}{(\lambda_j - \lambda_i)s_j}, \quad (13) $$
\[ s_i = y_i^T x_i, \]  
\[ \beta_{ij} = y_i^T A_1 x_j, \]  

where \( y_i; x_i \) are respectively the left and the right eigenvectors.

Let \( H(r) \) be a Hamiltonian matrix of some fixed state of molecular system. Let us then consider a perturbation of Hamiltonian matrix \( H(r) \) which corresponds to a shift of \( l \)-th component of \( i \)-th position vector of the system by \( \delta \) in the following form:

\[ H_{il}^\delta (r) \delta = H(r + e_i \delta) - H(r), \]  

Generic form of Hamiltonian matrix elements is as follows:

\[ h_{pq}(r_1, r_2, ..., r_N), \]  

where \( h_{pq}(r_1, r_2, ..., r_N) \) are differentiable.

Then we can write elements of \( H_{il}^\delta (r) \) matrix as

\[ h_{ilpq}(r_1, ..., r_l - e_l \delta, ..., r_N) - h_{ilp}(r_1, ..., r_N), \]  

where \( e_l \) is a vector directed as the \( l \)-th axis of cartesian coordinate system. Using Taylor series expansion we obtain

\[ H_{ilpq}^\delta (r) = \left( \frac{\partial h_{pq}(r_1, ..., r_N)}{\partial r_{il}} \delta + O(\delta^2) \right) / \delta. \]  

Dividing by \( \delta \) we finally get

\[ H_{il}^\delta (r) = \frac{\partial H(r)}{\partial r_{il}} + E0(\delta), \]  

where \( \partial H(r)/\partial r_{il} \) is an element-wise partial differential of \( H(r) \) matrix by \( l \)-th coordinate of position vector of \( i \)-th atom, and \( E \) is an identity matrix.

Using (11) we derive that

\[ e_n(r + e_i \delta) = e_n(r) + k_1^n \left( H_{il}^\delta (r) \right) \delta + k_2^n \left( H_{il}^\delta (r) \right) \delta^2 + \cdots, \]  

or, equivalently,

\[ e_n(r + e_i \delta) - e_n(r) = k_1^n \left( H_{il}^\delta (r) \right) \delta + k_2^n \left( H_{il}^\delta (r) \right) \delta^2 + \cdots, \]  

If we divide (22) by \( \delta \) and send \( \delta \) to zero we will have

\[ \lim_{\delta \to 0} \frac{e_n(r + e_i \delta) - e_n(r)}{\delta} = \lim_{\delta \to 0} \left\{ k_1^n \left( H_{il}^\delta (r) \right) \delta + k_2^n \left( H_{il}^\delta (r) \right) \delta^2 + \cdots \right\}, \]  

Because \( k_1^n \) are coefficients of convergent series, they are bounded, so we have

\[ \frac{\partial e_n(r)}{\partial r_{il}} = \lim_{\delta \to 0} k_1^n \left( H_{il}^\delta (r) \right). \]  

Using (12) we obtain the following equation:

\[ k_1^n \left( H_{il}^\delta (r) \right) = \frac{\beta_{an} \left( H_{il}^\delta (r) \right)}{s_n}, \]
Because Hamiltonian matrix is symmetric, its left and right eigenvectors coincide, and norm of each equals to 1. Hence, using (14) we can infer that \( s_n = 1 \).

Finally we have

\[
k_l^n \left( H_l^n (r) \right) = \beta_{nn} = x_n^T \left( \frac{\partial H(r)}{\partial r_{il}} + EO(\delta) \right) x_n,
\]

from which follows that

\[
\frac{\partial \varepsilon_n(r)}{\partial r_{il}} = \lim_{\delta \to 0} \left\{ x_n^T \frac{\partial H(r)}{\partial r_{il}} x_n + x_n^T E x_n O(\delta) \right\},
\]

But we \( x_n^T E x_n = x_n^T x_n = s_n = 1 \) we obtain that

\[
\frac{\partial \varepsilon_n(r)}{\partial r_{il}} = \lim_{\delta \to 0} \left\{ x_n^T \frac{\partial H(r)}{\partial r_{il}} x_n + O(\delta) \right\},
\]

The first expression inside the limit operator does not depend on \( \delta \), and the second one vanishes as \( \delta \to 0 \), so the following equation holds:

\[
\frac{\partial \varepsilon_n(r)}{\partial r_{il}} = x_n^T \frac{\partial H(r)}{\partial r_{il}} x_n
\]

Therefore in order to find gradient of \( E_{\text{bond}} \) it is enough to know only eigenvectors and element-wise partial derivatives of Hamiltonian matrix at \( r \).

We developed the molecular dynamics simulation algorithm in the framework of the hybrid method 'hot spot' with construction of the local stress map:

1. Minimization of the total energy of the initial system in the framework of the quantum method.
2. The finding of the volume energy density \( \omega^0_l \) for the initial state of the system.
3. The calculation of the volume energy density for the current state of the system.
4. The construction of the local stress map for the current state of the system.
5. The analysis of the local stress map and the determination of the list of the atoms in the active zone.
6. The construction of the hot region the components of strong connectivity in graph, consisted of the atoms of the active area using the Tarjan algorithm.
7. The construction of Hamiltonians for each hot region and the calculation of their eigenvectors.
8. The calculation of the forces, acting on the atoms, entering in hot regions, according to formula (29).
9. The calculation of forces, acting on the atoms of the system by the molecular mechanics method(REBO).
10. The finding the forces, acting on the atoms of the system in the framework of the 'hot spot' method by formula (2).
11. The calculation of the coordinates for atoms at the next time step.
12. The return to the item 3 for the realization of the next step of molecular dynamics.
4. Approbation of the developed algorithm for determination of the active zone boundaries in the framework of the hybrid method QM/MM

The test problem, concluded in the study of the behavior of carbon nanotube with double vacancy defect, was resolved to verification of the developed algorithm for determination of the active area boundaries. Our aim consisted in that to correctly predict the area of the object destruction, and also to establish the regularities of the local stress distribution on the atoms, formed the active zone. The nanotube of zigzag (10,0) was chosen as an object of the investigation. As a result of investigation it was established that the breaking of C-C bonds was registered for the first time in the defect area at the tension of structure on 19%. The scanning of the local stress map for defected nanotube was shown that the maximum stress was concentrated on the atoms exactly in this structure fragment (see Fig. 3). The red color corresponds to the maximum values of the stress (70 GPa). The blue color corresponds to the minimal values of the stress (less of 1 GPa). Consequently, the active region boundaries were identified correctly. Atomic structure of nanotubes with double vacancy defect at the moment of the fracture is shown in Fig. 4.

![Fig. 3. The distribution of the local stress on the atoms of the deformed zigzag carbon nanotube at the moment before destruction.](image)

![Fig. 4. The atomic structure of zigzag carbon nanotube at the moment of destruction.](image)

5. Conclusion

The theory of algorithm for dynamical determination of the active zone in the framework of the hybrid method (QM/MM) is developed in the current investigation for the first time. This algorithm is based on the procedure of finding of the stress on the atoms of the investigated structure. The scanning of the local stress map allows to dynamically determinate the active and buffer zones in compliance with change of the system state in time. The approbation of the developed algorithm is performed on example of solution of the test problem. This problem is the modeling of the tension of zigzag carbon nanotube. The results of a calculation showed a high efficiency of the proposed algorithm. Using a hybrid method (QM/MM) with the original algorithm of dynamic determination of the active region one can model the behavior of the multi-atomic molecular systems subjected to mechanical loads, and also perform the simulation of the work for different functional devices based on them.
References


