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Parallel algorithms for solving of multidimentional vibrational Shrödinger equation

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1. Introduction

Computational quantum mechanical methods are widely used for investigation of molecular electronic structure, dynamical properties of many atomic structures, chemical reactions. In order to achieve quantitative results comparable with experimental we need supercomputer's power or parallel computers cluster. The cluster have been created in Applied Sciences Department in Lithuanian Military Academy [1]. Created computational facilities were applied to investigate electronic structure and vibrational spectra of trinitrotoluene molecule by means of non-empirical quantum mechanical computational methods. The accurate nonempirical quantum chemical computations are essential in development of spectroscopic methods for detection of small amounts of materials. The effective usage of parallel computers is only possible using effective parallel algorithms. In our paper we describe the possibility to parallelize algorithm for solving of vibrational Shrödinger equation by means of self consistent field method.

2. SCF vibrational equations

Hamiltonian of many atomic molecule in normal coordinates Q for molecular rotational quantum number $J = 0$ have the form

$$\begin{aligned}\widehat{H} &= \frac{1}{2}\sum_{\alpha,\beta}\mu_{\alpha\beta}\pi_\alpha\pi_\beta + \frac{1}{2}\sum_{k=1}^{N}P_k^2 - \frac{\hbar^2}{8}\sum_{\alpha}\mu_{\alpha\alpha} + V(Q)\\ &= T_{cor} + T_{vib} + T_{rot} + V(Q),\end{aligned} \tag{1}$$

here N – number of normal modes, α and β – components of Cartessian x, y, z coordinates, $\mu_{\alpha\beta}$ – components of inverse effective inertia tensor, π_α – Cartessian component of vibrational angular momentum. It have the form

$$\pi_\alpha = \sum_{i>j}\xi_{ij}^{(\alpha)}(Q_iP_j - Q_jP_i). \tag{2}$$

Vibrational part of hamiltonian have the form

$$\widehat{H}_{vib} = \sum_{k=1}^{N} P_k^2/2\mu + V(Q_1, \ldots, Q_N), \tag{3}$$

here Q_i – normal coordinate and P_i – corresponding angular momentum, μ_i – reduced mass of many particle system, N – total number of vibrational modes.

$$V(Q_1, \ldots, Q_N) = \frac{1}{2} \sum_{i=1}^{N} k_i Q_i^2 + W_{anh}(Q_1, \ldots, Q_N), \tag{4}$$

here k_i – force constant of the i-th normal mode, W_{anh} – unharrmonic part of potential describing coupling of normal modes.

Usually W_{anh} is presented as higher order (3-rd, 4-th, . . .) terms in Tailor expansion. When we consider vibrations of small amplitudes higher order than quadratic terms in potential energy expansion (4) may be neglected. Then vibrational hamiltonian of molecule is the sum of hamiltonians of harmonic oscilators $\omega_i = (k_i/\mu_i)^{1/2}$. W_{anh} member can't be neglected when high amplitude vibrations or excited vibrational states are investigated. This can be accomplished by means of self-consistent field method. Initial molecule's wavefunction in harmonic approximation ($W_{anh} = 0$) may be written in the form

$$\Psi(Q_1, \ldots, Q_N) = \prod_{I=1}^{N} \Psi_I(Q_i), \tag{5}$$

here $\Psi_i(Q_i)$ describes i-th state of Q_i-th normal mode.

Application of variation principal

$$\delta \left\{ \langle \Psi | \widehat{H} | \Psi \rangle / \langle \Psi | \Psi \rangle \right\} = 0 \tag{6}$$

leads to the system of equations

$$\left(h_{ef}(i) - \varepsilon_i\right) \Psi_i(Q_i) = 0, \quad i = 1, \ldots, N, \tag{7}$$

which is usually solved by iteration method.

Effective hamiltonian has the form

$$\begin{aligned} h_{ef}(i) &= P_i^2/2\mu + V_i(Q_i) + \left\langle \prod_{j \neq i}^{N} \Psi_j(Q_j) \, | W_{anh}(Q_1, \ldots, Q_N) | \prod_{j \neq i}^{N} \Psi_j(Q_j) \right\rangle \\ &= P_i^2/2\mu + V_i(Q_i) + V_{SC}(Q_i). \end{aligned} \tag{8}$$

The i-th mode self consistent (SC) potential $V_{SC}(Q_i)$ is derived from molecule's full potential after averaging according to all normal modes. In order to find wave function

$\Psi_i(Q_i)$ it is necessary to solve the system of N equations by iteration method. Full vibrational energy of molecule equal:

$$E = \sum \varepsilon_i^{SC} - (N-1)\left\langle \prod_{j\neq i}^{N} \Psi_j^{SC}(Q_j) \, | V_{SC}(Q_1, \ldots, Q_N) | \prod_{j\neq i}^{N} \Psi_j^{SC}(Q_j) \right\rangle, \quad (9)$$

here ε_j^{SC} and Ψ_j^{SC} – solutions of self consistent equations.

We have to solve equations by self consistent field method in two steps:

1) to solve one dimensional differential equations of 2-nd order (7),

2) computation of $(N-1)$-dimension integrals in order to find effective potential $(V_{SC}(Q_i))$. So, we have changed one N dimentional differential equation to N one dimentional equations. This enables us to use parallel computations.

Necessary computer processor's time have linear dependence from N. When solving the same equation by means of variational method and expanding wave function in the basis of harmonic oscillators CPU time grows faster. Self consistent field solving parallel algorithm of one dimensional Shrödinger equation is described in [2].

Another algorithm for first-principles calculation of vibrational spectroscopy of polyatomic molecules was proposed [3], which combines electronic *ab initio* codes with the vibrational self-consistent field (VSCF) method, and with a perturbation-theoretic extension of VSCF. The integrated method directly uses points on the potential energy surface, computed from the electronic *ab initio* code, in the VSCF part. No fitting of an analytic potential function is involved. A key element in the approach is the approximation that only interactions between pairs of normal modes are important, while interactions of triples or more can be neglected. Unfortunately at this time only 10–15 atom molecules can be treated by this method because of very computer time consuming potential energy surface computations.

3. Vibrational spectra computations

Trinitrotouluene molecule vibrational spectra computations were performed using computer code GAMESS [4]. For potential energy surface determination in Hartree–Fock (HF) approximation atomic orbital (AO) basis 6–31G* (total 250 basis functions) was used. Number of necessary to compute many center integrals was more than 10^9.

Nonempirical calculation of harmonic vibrational spectra in HF approximation took about 40 min. of clusters CPU time. In Table 1 we present vibrational frequencies of trinitrotoluene molecule. Computation of points on potential surface (for VSCF) even at HF level was very computer time consuming. We could compute only 8 points along each normal mode and interaction between modes was neglected. It is quite rood approximation. It should be mentioned, that SCF calculation of vibrational spectra took very small amount of clusters facilities in comparison with potential enegy surface calculation.

Presented results are of quite pour accuracy. The main inaccuracy is from potential energy surface evaluation. For molecules of media size (like tritrotoluene) this can be

Table 1

2,4,6-Trinitrophenol molecule unharmonic vibrational frequencies calculated by vibrational self consistent field method [3]. Unharmonicity of potential energy surface along normal modes only was regarded. Potential surface was calculated in HF approximation in 6-31G* basis. Only most intensive modes are presented

Harmonic [5]		Diagonal SCF
Frequency, cm^{-1}	IR intensity, D**2/a.m.u-A**2	Frequency, cm^{-1}
3348.31	0.63834	3123.05
2583.51	2.52890	2016.19
2180.10	8.35142	1483.23
1923.09	12.92500	1615.28
1852.33	5.38627	1819.30
1819.39	7.70223	1734.63
1743.60	17.68548	1700.75
1619.05	2.28316	1481.65
1560.38	2.94315	1558.27
1428.95	1.82790	1464.54
1322.81	0.51712	1361.71
1132.08	0.00918	1136.76
1128.34	2.21725	1204.47
1109.83	0.41348	1111.80
1026.44	1.29588	1056.13
932.30	1.51777	1052.87
894.50	0.54349	1047.29
854.63	0.51690	843.75
814.89	1.26546	801.87
804.38	0.31846	790.72
768.82	0.34285	1020.11
754.07	0.00987	741.97

afforded by strait increase of clusters performance. For extremely large molecules (biological) another methods (empirical) should be used for potential energy surface determination. In latter case vibrational equations system grows large and parallelisation of vibrational SCF algorithm will be essential.

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DAUGIAMATĖS VIRPESINĖS ŠREDINGERIO LYGTIES SPRENDIMO LYGIAGRETIEJI ALGORITMAI

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Kompiuterizuotieji kvantinės mechanikos metodai yra plačiai naudojami molekulių elektroninei struktūrai, spektrams ir dinaminėms savybėms tirti. Tokiems skaičiavimams reikalingi superkompiuteriai arba lygiagrečiųjų skaičiavimų kompiuterių klasteriai. Darbe pateikiamas lygiagrečiųjų skaičiavimų algoritmas didelių molekulių virpesiniams spektrams apskaičiuoti, daugiamatę virpesinę Šredingerio lygtį sprendžiant suderintinio lauko metodu normaliųjų koordinačių bazėje. Lietuvos karo akademijos lygiagrečiųjų skaičiavimų klasterio galimybės įvertintos skaičiuojant trinitrotoluolo molekulės virpesinį spektrą suderintinio lauko metodu, naudojant skaitmeninį potencinės funkcijos pavidalą bei neatsižvelgiant į sąveiką tarp normaliųjų svyravimųų. Gautieji rezultatai rodo, kad didelėms molekulėms tirti minėtais metodais reikalinga didinti klasterio našumą bei kurti efektyvesnius lygiagrečiųjų skaičiavimų algoritmus.