Fragmentation method combined with Quantum Monte Carlo calculations

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The total energy of a small polypeptide system is calculated by combining the quantum Monte Carlo (QMC) and fragment molecular orbital (FMO) methods. Electronic correlation is taken into account using Slater-Jastrow wave functions and the variational quantum Monte Carlo (VMC) method. We calculate the energy of the whole system directly and by using the FMO method, finding that the combined QMC-FMO approach works very well.

KEYWORDS: *ab initio*, FMO, QMC, Biomolecule, polypeptide, Order-N

1. Introduction

One of the recent trends in *ab initio* electronic structure computations has been the interest in calculations for large low-symmetry systems, which leads to great computational expense, both in terms of CPU and memory requirements. Methods for reducing the computational expense normally involve dividing the system up in some way.

Recently developed order-N methods[1,2)] for insulators rely on the exponential localization of the one-particle density matrix, so that distant points can be considered separately. Another possibility is to divide the systems into fragments and reconstruct quantities such as the energy and the electronic charge distribution of the whole system from those of the fragments. Suitable fragmentations can be devised for a number of systems, including many biosystems, which are of particular interest. Fragmentation is a rather simple idea which can be implemented within standard electronic structure codes with rather few modifications. Other approaches such

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as embedding methods,[3] effective medium methods[4] and Quantum Mechanical/Molecular Mechanical (QM/MM) schemes[5] share the same basic idea of an effective treatment of the interaction with surrounding regions.

QMC methods have recently been developed which use the idea of the exponential localization of the one-particle density matrix within insulators[6,7] but, so far, no QMC calculations using the fragmentation approach have been reported. Within the fragmentation approach the task of performing a calculation for a large system is broken down into a number of smaller calculations. The fragment molecular orbital (FMO) approach of Kitaura *et al.*[8–10] is one of the most successful fragmentation methods. It incorporates well-established rules for determining accurate fragmentations which, within the Hartree-Fock (HF) approximation, result in deviations in the energy from the full calculation of only a few kcal/mol for typical polypeptides and proteins. One may be sceptical that such an artificial division of the system might lead to a significant error in the total energy, but when applied to suitable systems it performs very well.

With the rapid increase in the availability of computational resources, there has been interest in combining the FMO technique with electronic structure methods beyond the HF level. A number of studies[11–13] combining Møller–Plesset (MP) perturbation theory and the FMO technique have been reported. Energies calculated at the MP2 level using the FMO approach are in very good agreement with MP2 energies for the whole molecule, showing that the FMO technique can work when electron correlation is included. However, the cost of an MP2 calculation increases as N^5, where N is the number of basis functions, and this approach is non-variational. The cost of a QMC calculation increases as N^3, where N is now the number of electrons in the system, and QMC techniques are variational.[14] QMC methods are generally well suited to parallel computation, but calculations for large systems become inefficient if the trial wave function is too large to be stored on each processor. The idea is that the FMO technique allows the division of the task of performing a calculation for a large molecule into a number of much smaller tasks which could be distributed among a number of researchers, who could each use relatively inexpensive local computational resources.

Here we report our attempt to combine the FMO and QMC methods. Taking a glycine trimer as a simple example, we have compared the ground state energy in the FMO approximation with the result obtained by the full treatment of the whole molecule. Although the FMO approximation has already been shown to work well at the HF and MP2 levels, QMC is a very different technique, and it is necessary to show that it can be successfully combined with the FMO before progressing to more challenging systems where it is impractical to perform the full calculation. We have developed a FMO-QMC technique and confirmed that it works well at the variational Monte Carlo (VMC) level. This is the first such attempt and it confirms the possibility of using FMO-QMC techniques to deal with large biomolecule complexes.

The plan of this paper is as follows. In § 2 we describe the system studied and its fragmentation. The molecular orbitals obtained from the HF self-consistent field (HFSCF) calculations are used in the trial wave functions for the QMC calculations. In § 3 we present the details of the VMC calculations. The VMC results without Jastrow correlations factors (HFVMC results) are compared with the HFSCF results in § 3-A, while § 3-B describes HFVMC calculations in which the basis set is effectively improved by including the proper electron-nucleus cusps in the orbitals. § 3-C describes the VMC calculations with Jastrow factors. We draw our conclusions in § 4.

2. System, Fragmentation, and HFSCF Calculations

2.1 Structure and fragmentation

We have considered a trimer of glycine, H_2N-CH_2-COOH, formed by peptide bonding, which contains three nitrogen, six carbon, four oxygen, and eleven hydrogen atoms, giving a system with 100 electrons. We optimized the geometry of the trimer at the HF level using the Gaussian98[15] code with an STO-3G Gaussian basis set, starting from an initial α-helix structure. The optimized structure is shown in Table I.

The art of fragmentation is well established for peptides and DNA.[10,16] At the HF and MP2 levels with an STO-3G basis, the accuracy has been established to within a few kcal/mol using the best empirically established dividing rule. In peptides it is considered best to divide each residue at the C_α site where one of the six electrons is transferred to the adjacent fragment.[10,16] In the present case the molecule is divided into three fragments (fr1, 2, and 3) at the sites 4 and 11 shown in Table I. The carbon at site 4 (11) is hence shared by fr1 and fr2 (fr2 and fr3) as shown in the table. The fragmentation is depicted schematically in Fig. 1.

Within the FMO method, the electronic energy ε is considered separately from the repulsive energy between the ionic cores $E_{\rm NN}$, so that the total energy is written as

$$E = \varepsilon + E_{\rm NN} \ . \tag{1}$$

The interaction energy between fragments I and J can be expressed as

$$\delta\varepsilon_{IJ}^{\rm int} = \varepsilon_{IJ} - (\varepsilon_I + \varepsilon_J) \ , \tag{2}$$

where ε_I and ε_{IJ} are the energies of each fragment and fragment pair calculated under the influence of the electrostatic potentials of all the other fragments. The electrostatic potential is evaluated from the charge density of each fragment obtained from HFSCF calculations. Within this approximation the electronic energy can be expressed as

$$\varepsilon_{tot}^{\rm (FMO)} = \sum_{I>J} \varepsilon_{IJ} - (N_{\rm F} - 2) \sum_I \varepsilon_I \ , \tag{3}$$

where $N_{\rm F}$ is the number of fragments. In the present case it reduces to

$$\varepsilon_{tot}^{\rm (FMO)} = \varepsilon_{12} + \varepsilon_{23} + \varepsilon_{31} - (\varepsilon_1 + \varepsilon_2 + \varepsilon_3) \ . \tag{4}$$

No.	Element	x	y	z	fragment
1	N	3.0862	-2.1940	0.4675	1
2	H	3.2786	-1.8310	1.4158	1
3	H	2.2117	-2.7340	0.5750	1
4	C	2.7797	-1.0290	-0.3930	1/2
5	H	3.6895	-0.4400	-0.5280	1
6	H	2.4655	-1.3810	-1.3770	1
7	C	1.6685	-0.1040	0.1810	2
8	O	1.1474	-0.2690	1.2689	2
9	N	1.2465	0.9411	-0.7220	2
10	H	2.0254	1.2783	-1.3010	2
11	C	0.5140	2.0642	-0.0990	2/3
12	H	1.0468	2.5058	0.7482	2
13	H	0.3868	2.8409	-0.8560	2
14	C	-0.8950	1.6371	0.4006	3
15	O	-1.4790	2.1933	1.3110	3
16	N	-1.4400	0.4951	-0.2870	3
17	H	-1.0580	0.3979	-1.2330	3
18	C	-2.9000	0.2935	-0.2070	3
19	H	-3.2760	0.8922	0.6253	3
20	H	-3.4180	0.6076	-1.1160	3
21	C	-3.2160	-1.2130	0.0723	3
22	O	-4.2970	-1.7270	-0.1330	3
23	O	-2.1550	-1.9350	0.5931	3
24	H	-1.4080	-1.2850	0.5996	3

Table I. Optimized structure of the glycine trimer. All coordinates are given in Angstroms. The column headed 'fragment' specifies the fragment to which the atom belongs, see Fig. 1.

2.2 HFSCF calculations

We used the ABINIT-MP code[16–18] for the HFSCF calculations, performing all-electron calculations with an STO-3G Gaussian basis set. The calculations for fr2 and fr3 included a 'floating basis' for a single carbon atom, as shown in Fig. 1.

Self-consistency of the FMO procedure is achieved when the total electronic charge density has converged. Within the FMO, the total charge density is given by

$$\rho_{tot}^{(\mathrm{FMO})} = \sum_{I>J} \rho_{IJ} - (N_F - 2) \sum_{I} \rho_I \ , \tag{5}$$

which is obtained in a similar way to eq. (3). Several levels of approximation of the electro-

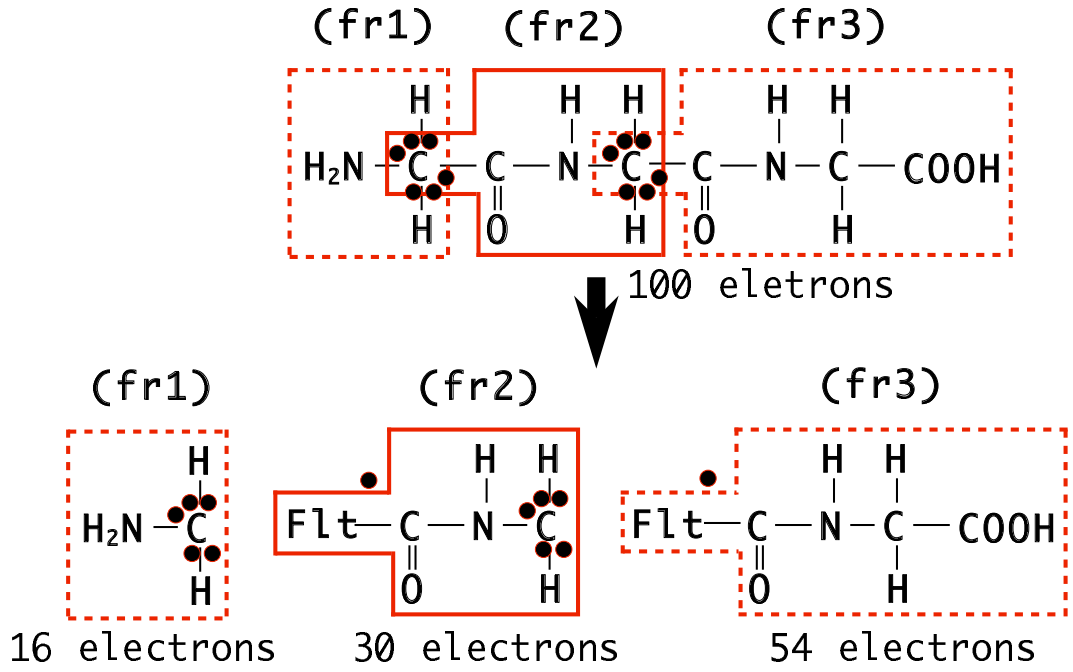

Fig. 1. (Color online) Schematic depiction of the fragmentation. 'Flt' indicates a carbon atom 'floating basis' with a central charge of $Z = 0$. The dots denote the electrons around the C_α atoms.

static potential are available in ABINIT-MP, but in this work we have not used any of the approximate schemes and have instead evaluated the Hartree integrals using the method of Obara and Saika.[19)]

The HFSCF results are shown in Table II. At the HF level, the total energy in the FMO approximation of −687.3874 a.u. is very close to the value of −687.3875 a.u. obtained in the full calculation. This high level of agreement is typical of that achieved in other FMO calculations for polypeptides.[16)]

3. VMC Results

In the VMC method the energy is evaluated as the expectation value of the Hamiltonian $\hat{H}$ with a many-body trial wave function, Ψ,

$$E = \frac{\int \Psi^* \hat{H} \Psi \, d\mathbf{R}}{\int \Psi^* \Psi \, d\mathbf{R}} = \frac{\int |\Psi|^2 \Psi^{-1} \hat{H} \Psi \, d\mathbf{R}}{\int |\Psi|^2 \, d\mathbf{R}} \tag{6}$$

where $\mathbf{R}$ is the $3N$-dimensional vector of the electron positions, and the energy has been recast as an average over the probability distribution $p(\mathbf{R}) = |\Psi|^2 / \int |\Psi|^2 \, d\mathbf{R}$. The energy expectation value is evaluated by Monte Carlo integration, using the Metropolis algorithm to generate points in the $\mathbf{R}$ space distributed according to $p(\mathbf{R})$. The statistical efficiency of the Monte Carlo integration improves as the quality of Ψ improves, because the local energy, $\Psi^{-1}\hat{H}\Psi$, becomes a smoother function of $\mathbf{R}$.

All of the QMC calculations were performed with the CASINO QMC code.[20)] The code was

	HFSCF (a.u.)	HFVMC (a.u.)	HFVMC (a.u.)	VMC (a.u.)
e-n cusp correction	No	No	Yes	Yes
ε_1	-122.7992	-122.97(8)	-123.56(1)	-123.901(3)
ε_2	-307.6071	-307.6(1)	-309.13(2)	-309.880(4)
ε_3	-683.4616	-683.1(2)	-686.32(3)	-687.861(4)
ε_{21}	-518.3114	-518.3(1)	-520.59(2)	-521.725(4)
ε_{31}	-885.1518	-885.4(2)	-888.83(3)	-890.566(4)
ε_{32}	-1218.9123	-1218.9(2)	-1223.40(3)	-1225.581(4)
E_{NN}	+821.1203	+821.1203	+821.1203	+821.1203
E^{FMO}	-687.3874	-687.9(4)	-692.69(6)	-695.11(1)
$E^{\mathrm{Full;SCF}}$	-687.3875			
$E^{\mathrm{Full;VMC}}$		-687.6(6)	-692.60(7)	-695.10(1)

Table II. Comparison of the full and FMO results. HFSCF denotes results from self-consistent field calculations at the HF level, HFVMC denotes VMC results obtained without a Jastrow factor, and VMC denotes the use of a Jastrow factor.

extended to include the contribution of the electrostatic potential from the other fragments. The electrostatic potential is evaluated as the sum of the potentials from the nuclei and a discretized summation of point electronic charge contributions from cubic boxes of side 0.2 a.u. We have performed calculations using the electrostatic potentials obtained both from the HFSCF charge density and from the correlated charge density, but the difference was smaller than the statistical error bars. This is consistent with the observation that the small contraction of the charge density due to the introduction of electron correlation should not significantly affect the electrostatic potential acting on distant positions.

3.1 HFVMC calculations

We first performed VMC calculations using a trial wave function consisting of the product of up and down-spin determinants of the HFSCF orbitals,

$$\Psi(\mathbf{R}) = D_{\uparrow}(\mathbf{R})\, D_{\downarrow}(\mathbf{R}). \tag{7}$$

The HFVMC calculations without cusp corrections should give the same results as the HF-SCF ones, apart from the statistical errors and any bias from the different treatment of the electrostatic potentials. Comparing the HFVMC results (without cusp corrections) with the HFSCF data given in Table II, we see that the agreement is good. The total energies from the SCF and VMC methods are within a single standard deviation for the full calculations, and within two standard deviations for the FMO calculation. The fragment and its pair energies show a similar level of agreement to the total FMO energies. This demonstrates that any bias

due to the treatment of the electrostatic potentials is reasonably small. The FMO and full HFVMC energies (without cusp corrections) agree to within error bars. Unfortunately the error bars on the HFVMC energies (without cusp corrections) are large because the quality of the trial wave function is poor.

3.2 Cusp-corrected HFVMC calculations

The HFSCF calculations reported above were performed with a relatively small basis set. While the basis set quality could readily be improved for the glycine trimer, for very large systems even HF calculations can be difficult with high quality basis sets. The basis set error in the HF energy can be substantially reduced by replacing the molecular orbitals in the region around the nucleus by a form which obeys the electron-nucleus cusp condition. It would also be possible to optimize the Gaussian coefficients and exponents directly within a QMC procedure, both with and without the Jastrow factor, although we have not attempted this here.

We have used the cusp correction procedure introduced by Ma *et al.*[21] A molecular orbital ϕ satisfies the electron-nucleus cusp condition if

$$\left.\frac{d\left\langle\phi\right\rangle}{dr}\right|_{r=0} = -Z\left\langle\phi(r=0)\right\rangle, \tag{8}$$

where $<\phi>$ denotes the spherical average of the orbital about the nucleus at $r = 0$, and Z is the nuclear charge. Within a small radius around each nucleus, the part of each molecular orbital arising from the s-Gaussian basis functions is replaced by a form which ensures that the electron-nucleus cusp condition is satisfied. This procedure significantly improves the quality of the HF molecular orbitals. The addition of cusp corrections lowers the HFVMC energy by 5.0(6) a.u. for the full calculation and 4.8(4) a.u. for the FMO calculation. The cusp corrections also improve the energies for each of the fragments and fragment pairs, as shown in Table II. The full and FMO HFVMC energies, calculated with cusp corrections, agree to within error bars, indicating that, as expected, the FMO approximation also works well at this level. The improvement in the molecular orbitals also substantially reduces the correlation length of the energy along the random walk and the variance of the energy, resulting in the reduction in the error bars apparent in Table II.

3.3 Slater-Jastrow trial wave functions

The Slater-Jastrow trial wave function is given by

$$\Psi\left(\mathbf{R}\right) = \exp\left[J\left(\mathbf{R}\right)\right] D_{\uparrow}\left(\mathbf{R}\right) D_{\downarrow}\left(\mathbf{R}\right), \tag{9}$$

where $\exp\left[J\left(\mathbf{R}\right)\right]$ is a Jastrow correlation factor. We used the cusp-corrected HF orbitals described above to form the determinants $D_{\uparrow}$ and $D_{\downarrow}$.

We used Jastrow factors of the form[22)]

$$J(\mathbf{R}) = \sum_{i>j} u(r_{ij}) + \sum_I \sum_i \chi_I(r_{iI}) + \sum_I \sum_{i>j} f_I(r_{iI}, r_{jI}, r_{ij}) \ , \tag{10}$$

where the indices i and j denote electrons and I denotes ions. The u term describes homogeneous, isotropic, electron-electron correlations, the χ term describes one-body isotropic electron-nucleus correlations, and the f term describes isotropic electron-electron-nucleus correlations. Each of the terms is represented as a power series in its arguments, and is chosen so as to enforce the electron-electron cusp conditions while maintaining the electron-nucleus cusp conditions. The three terms are cut off smoothly at distances of $L_u = 5.0$ a.u., $L_\chi = 4.0$ a.u., and $L_f = 3.0$ a.u., respectively. By keeping the number of variable parameters and the cutoff lengths the same for all calculations we hope to construct Jastrow factors of equal quality for each calculation.

The coefficients in the power expansions are determined by minimizing the self-consistent unreweighted variance of the energy using a VMC procedure. As the coefficients appear linearly in the Jastrow factor, the optimization can be performed efficiently using the scheme devised recently by Drummond *et al.*[23)]

The FMO-VMC energy of $-695.11(1)$ a.u. and the full-VMC energy of $-695.10(1)$ a.u. agree within error bars, demonstrating that the FMO method works well at the correlated VMC level. The statistical error bars on the correlated VMC energies are much smaller than those for the HFVMC results because the correlated wave functions are much more accurate.

The computational cost of the FMO-QMC calculations is also a matter of interest. The FMO-QMC approach is not expected to be very efficient for the system studied here because of its small size, but it turns out that using precisely the same methodology in an FMO-QMC calculation for a large system would also be inefficient. The problem is that the evaluation of the FMO energy expression of eq. (3) for a system of N_F fragments requires a total number of calculations proportional to N_F^2, as one must consider both the fragments and the fragment pairs. Because each of the calculations is independent, the total statistical error is equal to the square root of the sum of the squares of the errors in the individual calculations. The cost of a QMC calculation is approximately proportional to the cube of the number of electrons (N^3), from which one can readily deduce that the present implementation of the FMO calculation actually requires more cpu time than the full calculation!

A more efficient methodology is therefore required for FMO-QMC calculations on large systems. Significant savings can be achieved for large systems by neglecting the correlations between distant fragment pairs, and in the most favorable case the total number of calculations required would be proportional to N_F rather than N_F^2. When N_F is sufficiently large this saving is already sufficient to make the FMO-QMC calculation more efficient than the full calculation.

Further efficiency gains can be made by employing correlated sampling techniques.[24)]

Writing the FMO energy of eq. (3) directly in terms of the interaction energies, we obtain

$$\varepsilon_{tot}^{(\mathrm{FMO})} = \sum_{I>J} \delta\varepsilon_{IJ}^{\mathrm{int}} + \sum_{I} \varepsilon_I \ . \tag{11}$$

It is clear from this expression that the FMO energy can be calculated within QMC using a correlated sampling approach for the interaction energies, $\delta\varepsilon_{IJ}^{\mathrm{int}}$. Correlated sampling can be implemented efficiently within VMC, and at the DMC level using the reptation QMC technique.[25] Combining FMO with QMC in this manner would provide a powerful and efficient technique.

The FMO-QMC formulation has some further advantages. Firstly, the FMO-QMC formulation requires trial wave functions only for fragments and fragment pairs, which are normally much smaller than the full system. Accurate trial wave functions for small systems are much more readily obtained than for large systems, and we would like to perform FMO calculations on some systems which are so large that the full calculation is not feasible. Secondly, the individual calculations in the FMO formulation are much smaller than the full calculation and require much less memory, so that they may be performed using smaller computational facilities.

4. Conclusion

The QMC ground state energy of a glycine trimer has been calculated within the FMO approximation and compared with that obtained by a full calculation, at the level of HFVMC with/without electron-nucleus cusp corrections, and at the VMC level with an optimized Jastrow function. The introduction of electron-nucleus cusp corrections significantly improves the quality of the molecular orbitals, reducing the correlation length of the energy along the random walk, the variance of the energy and the energy itself. The energies from the FMO and full calculations agree within the statistical energy bars at each level of theory. We have demonstrated that the FMO approximation works well within a variational explicitly correlated wave function technique. The FMO-VMC technique will become efficient for large systems if it is possible to neglect the correlations between distant fragments and/or if the interaction energies are evaluated using a correlated sampling technique. We also intend to examine the accuracy of the FMO approximation using the more sophisticated and accurate diffusion quantum Monte Carlo (DMC) technique.

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References

1) C.-K. Skylaris, P. D. Haynes, A. A. Mostofi, and M. C. Payne: J. Chem. Phys. **122** (2005) 084119.
2) P. Ordejón, D. A. Drabold, M. P. Grumbach, and R. M. Martin: Phys. Rev. B **48** (1993) 14646 ; *ibid.* **51** (1995) 1456 , and references therein.
3) J. E. Inglesfield: J. Phys. C **14** (1981) 3795 ; J. R. Trail and D. M. Bird: Phys. Rev. B **62** (2000) 16402 .
4) J. K. Nørskov and N. D. Lang: Phys. Rev. B **21** (1980) 2131; K. W. Jacobsen, J. K. Nørskov, and M. J. Puska: Phys. Rev. B **35** (1987) 7423; K. Stokbro, N. Chetty, K. W. Jacobsen, and J. K. Nørskov: Phys. Rev. B **50** (1994) 10727.
5) J. Gao and D. G. Truhlar: Ann. Rev. Phys. Chem. **53** (2002) 467 , and references therein.
6) A. J. Williamson, R. Q. Hood, and J. C. Grossman: Phys. Rev. Lett. **87** (2001) 246406.
7) D. Alfè and M. J. Gillan: J. Phys. Condens. Matter **16** (2004) L305.
8) K. Kitaura, T. Sawai, T. Asada, T. Nakano, and M. Uebayasi: Chem. Phys. Lett. **312** (1999) 319.
9) K. Kitaura, E. Ikeo, T. Asada, T. Nakano, and M. Uebayasi: Chem. Phys. Lett. **313** (1999) 701.
10) D. G. Fedorov and K. Kitaura: *Modern Methods for Theoretical Physical Chemistry of Biopolymers*, edited by E. B. Starikov, J. P. Lewis, and S. Tanaka (Elsevier, Amsterdam, 2006), pp.3-38.
11) D. G. Fedorov and K. Kitaura: J. Chem. Phys. **121** (2004) 2483.
12) Y. Mochizuki, S. Koikegami, T. Nakano, S. Amari, and K. Kitaura: Chem. Phys. Lett. **396** (2004) 473.
13) Y. Mochizuki, T. Nakano, S. Koikegami, S. Tanimori, Y. Abe, U. Nagashima, and K. Kitaura: Theor. Chem. Acc. **112** (2004) 442.
14) W. M. C. Foulkes, L. Mitas, R. J. Needs, and G. Rajagopal, Rev. Mod. Phys. **73** (2001) 33.
15) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, Ö. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komáromi, R. Gomperts, R. L. Min, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople: *Gaussian 98* (Gaussian, Inc., Pittsburgh, PA, 1998).
16) T. Nakano, T. Kaminuma, T. Sato, K. Fukuzawa, Y. Akiyama, M. Uebayasi, and K. Kitaura: Chem. Phys. Lett. **351** (2002) 475.
17) T. Nakano, Y. Mochizuki, K. Fukuzawa, S. Amari, and S. Tanaka: *Modern Methods for Theoretical Physical Chemistry of Biopolymers*, edited by E.B. Starikov, J.P. Lewis, and S. Tanaka (Elsevier, Amsterdam, 2006), pp.39-52.
18) `http://www.fsis.iis.u-tokyo.ac.jp/en/result/software.`
19) S. Obara and A. Saika: J. Chem. Phys. **84** (1986) 3963.
20) R. J. Needs, M. D. Towler, N. D. Drummond, and P. López Riós: CASINO *version 2.0 User Manual*, (University of Cambridge, Cambridge, 2006).
21) A. Ma, N. D. Drummond, M. D. Towler, and R. J. Needs: J. Chem. Phys. **122** (2005) 224322.

22) N. D. Drummond, M. D. Towler, and R. J. Needs: Phys. Rev. B **70** (2004) 235119.
23) N. D. Drummond and R. J. Needs: Phys. Rev. B **72** (2005) 085124.
24) M. H. Kalos and P. A. Whitlock: *Monte Carlo Methods, Vol. I* (Wiley-Interscience, New York, 1986).
25) S. Baroni and S. Moroni: Phys. Rev. Lett. **82** (1999) 4745.