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On the Correspondence between Molecular Orbital Energies and Empirical Force Field Potential Terms

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In order to avoid the difficulty associated with the parameterization of molecular mechanics (MM) potential functions for molecules containing hetero-atoms, a possibility of switching the standard from experimental to theoretical is suggested. Advantages and disadvantages of the *ab initio* MO-based, transferable force field are discussed. As the first step toward this goal, the correspondence between the MM potential energy terms and quantities resulting from molecular orbital (MO) calculations has been investigated with the emphasis on extracting the general trend. Stretch, angle bending and electrostatic interaction energy terms can be computed without serious difficulties by MO methods. It is suggested that nonbonded interactions by the through-bond mechanism, especially of the 1,4-type, have been overlooked in the existing MM schemes. Prospects of improving the performance of MM by incorporating these and other features are discussed.

INTRODUCTION

The current popularity of the molecular mechanics (MM) potential energy minimization method[1] appears to rest on the fact that it provides a handy 'computerized molecular model'. The constituent potential energy terms, and hence the interpretation of the computed results, well correspond to the chemists' idea of the molecule, as envisaged from manipulating framework models.[2] Furthermore, most of the inconveniences of molecular models, like fixed bond lengths and valence angles, either free or frozen bond rotation, and unrealistically hard contacts between nonbonded atoms, are removed and a number of features that can never be realized in conventional models, such as the attractive van der Waals interaction and geometry optimization, have been implemented in MM.[1] The results of MM calculations can be conveniently appreciated on the color graphic display which allows rotations, enlargements, contractions and other operations in real time.[3]

Nevertheless, practical as well as conceptual difficulties persist in the currently available MM methods.[4] The greatest practical problem is the paucity of parameters for hetero-atoms, and this arises from the dearth of reliable experimental data on the structures and energies of hetero molecules, against

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which the MM potential parameters are to be gauged. These data are being accumulated at such a slow rate that we cannot hope to obtain a truly versatile, yet reliable, empirical force field in the foreseeable future.

One way to avoid the hetero-atom problem will be to reconstruct the MM scheme entirely on the theoretically derived molecular force fields. With the recent rapid progress in molecular orbital (MO) methods[5–7] equipped with the gradient-type geometry optimization technique,[8,9] theoretical calculations of vibrational spectra, and hence of intramolecular force field, are quickly improving, even though the calculated vibrational frequencies still have to be scaled to achieve a reasonable fit with the observed values.[10] Especially, the *ab initio* calculations indeed reproduce equilibrium geometries with surprisingly high accuracies,[8] and perhaps relative energies as well.[11] We consider this method to be the one of choice for producing the transferable force field.

There are reservations, however, which discourage the immediate launching of a project that aims at constructing the transferable force field based entirely on *ab initio* MO results. The most serious objection is the empirical nature in choosing the basis set and other features.[12] To make the situation complex, a very large basis set and extensive correction for electron correlation do not necessarily guarantee better results of this method.[12,13] Hence, the preparation of a 'computed' standard set for molecular mechanics parametrization must be preceded by a careful search for computational conditions that provide results appropriate for our particular purpose. Despite these problems, the transferable *ab initio* MO-based force field that we propose has several advantages over the totally empirical force field constructed to reproduce experimental values:

(1) Even if the standard set of molecular properties obtained by *ab initio* calculations might involve certain defects, these are likely to be uniform and may be corrected when the sources of defects are known.

(2) The *ab initio* force field is free from the ambiguity in the definition of geometry in the purely empirical force field, giving only r_e values.[14]

(3) The geometries in the *ab initio* force field correspond to the motionless state at the zero absolute temperature. Hence, it is a straightforward matter to correct the computed results for zero-point energy and thermal agitation effects and to add nonpotential terms.[15]

Two pioneering works closely related to our topics should be mentioned at this point. One is paper by Giunchi and Barino,[16] wherein a general hydrocarbon force field is constructed using energies and structures obtained from *ab initio* 4-31G calculations as the standards to be reproduced. The resulting force field, albeit a very simple one, appears to perform as well as the existing 'experimental' force fields and certainly encourages similar projects. The other is Bartell's paper,[17] wherein quadratic and cubic force constants of ethane have been derived from *ab initio* 4-31G calculations and the former compared with those of MM force constants. This work was the first serious attempt to correlate MO-calculated quantities with the properties of the empirical force field and clearly demonstrated how many important force constants were neglected in the existing MM schemes. Though Bartell[18] later developed the 'modified Urey-Bradley' (MUB) force field series based on this work, the MUB's are still of an extensively truncated type.

A new feature, emerging from the recent growth in computer technology, is that the MM force field does not have to be oversimplified any more in order to save computer memory and time, as was demanded at the time when most of the presently used force fields were written. It certainly appears true that all the existing MM schemes, including MUB, are too simple to represent adequately the real molecular force field, containing, on the average, only six to eight potential functions. The CPU-demanding job of optimizing potential parameters should also be executed more frequently at places where the super-fast main-frame computer is available. Therefore, the forthcoming general force field, either MO-based or experiment-based, will contain a much greater number of potential terms and force constants, and more elaborate methods of searching stationary points. (On the other hand, the presently available force fields and their programs will find use in personal computers which are being rapidly upgraded regarding memory space and computing speed.)

Conceptual ambiguities existing in the MM scheme are also problem. One of the objections to the MM method in general pinpoints the lack of systematic and logical evolution, like that observed with the MO method. The well-known fact that various existing MM schemes, differing significantly in terms of the number and form of potential functions, usually give good equilibrium structures and conformational energies, indicates that the MM potential terms may not be independent but correlated with each other and that the distribution of intramolecular force among potential terms may have been achieved more or less successfully within the relatively small standard set of each MM scheme. This means that the force constants in different MM schemes *may not be transferable!* Under such circumstances, before starting the construction of a preliminary *ab initio* MO-based force field, we began an extensive study to seek correspondence between the quantities obtained by MM and MO calculations. We were soon surprised to realize that the interactions between these two powerful computational methods were limited to the occasional utilization of quantum chemically derived quantities, such as charge distribution for parameterization,[19] the use of MM optimized structure as fixed or initial input for MO calculations,[20] and the alternate[21] or parallel[22] uses of both methods for special purposes. The subsequent part of this paper describes the results of the initial phase of the correspondence study carried out by one of us (T. H.).

COMMENTS ON MO METHODS

MO methods can be classified into two groups: *ab initio* and semiempirical. Contrary to the MM method, both MO methods are without ambiguity in the underlying concepts. The *ab initio* MO scheme is simple in idea exactly because it is *ab initio*.[*2] The following points should be kept in mind for our purpose:

(a) A large basis-set dependence is observed. Equilibrium geometry can be correctly predicted within the Hartree-Fock level when polarization functions are added to the basis-set of double-zeta quality. The charge distribution is almost satisfactorily predicted at this level of calculation, as judged from the comparison of the calculated with the measured dipole moments in the

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[*2] It does not mean that the *ab initio* MO is free of parameterization as long as we use Gaussian expansion of the exact wavefunctions.

gas phase.*[3,4] For polar molecules, however, electron correlation should be included, as it was discussed for 1,2-difluoroethane.[25] It follows that the calculations are limited to very small molecules.

(b) The *ab initio* MO packages available at present, GAUSSIAN 80[26] for example, give very little information, excepting total energy, Mulliken population analysis and dipole moment. Coding is necessary to derive the other properties from the calculated eigenfunctions.[27]

(c) In the *ab initio* MO scheme, the partition of the total molecular energy to »atoms and atom-pairs« is impossible, as a rule, due to the presence of the electron repulsion integrals over three and four atom-centers. The absolute magnitudes of the three- and four-centered energy terms are quite small (less than 1.2% of the total energy in the case of ethane).[28] Nevertheless, these terms cannot be neglected since their changes in conformational energies of ethane are of comparable order to the change of the total two-center energy and greater than the change of the total energy itself.[28,29] The significance of three- and four-center terms calculated by the *ab initio* MO is a substantial objection in the use of this method for calibration of MM terms which are basically two-centered, *i. e.* pair-wise additive, even though angle deformation is a three-center term and torsion may be regarded as a four-center term.*[5] There is however, no reason, for adamantly assuming the pair-wise character for the MM potentials.

Semiempirical MO methods, such as the CNDO/2,[20] INDO,[31] MINDO/1 to 3,[32–34] and MNDO,[35] are constructed to reproduce the observed properties of up to two-centers. The electron correlation effect is implicitly included through the parameters. As shown by Pople *et al.* for the CNDO method,[30,36] the total energy E of any MO method using only one- and two-center integrals can be reduced to its components as

$$E = \sum_{i} E_i + \sum_{i<j}\sum E_{ij} \tag{1}$$

$$E_{ij} = E_{\text{res}} + E_{\text{exc}} + E_{\text{el}} \tag{2}$$

where E_i and E_{ij} are one- and two-center energies, and E_{res}, E_{exc} and E_{el} are the resonance, exchange and electrostatic terms, respectively.[37] This feature is the strong point of the semiempirical MO scheme for the comparative study of MO and MM energy terms. The only, but fatal, drawback, however, is the *ad hoc* dependence of results on the parameters and the implemented approximations.

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*[3] Examples obtained at the 6-31G** level (in debye):

	Calc.	Obs.
Water	2.15	1.85
1,2-Difluoroethane	2.87	2.67

*[4] While dipole moments need not necessarily be considered as the best measure of the spatial charge distribution, combination of the Penning ionization electron spectroscopy[23] and the gas-phase NMR technique[24] should yield more detailed information on this quantity.

*[5] The neglect of intermolecular three- and four-center MO integrals will not cause serious errors in the intermolecular MM potentials. Total energies obtained by *ab initio* calculations have been successfully used to obtain intermolecular potentials, for example for simulating S_N2 reaction profiles in the gas and liquid phases: J. Chandrasekhar, S. F. Smith, and W. L. Jorgensen, *J. Amer. Chem. Soc.* **106** (1984) 3049.

SUGGESTED IMPROVEMENT OF MM SCHEME

Conformational energy E can be expressed in the MM scheme as

$$E = \Sigma E_v + \Sigma E_d + \Sigma E_{el} + \Sigma E_{nb} + \Sigma E_{rot} \quad (3)$$

where E_v, E_d, E_{el}, E_{rot} and E_{nb} are stretching, angle-deformation, electrostatic, torsional and nonbonded interaction terms, respectively, and the summations extend over appropriate atom pairs in the molecule. We will discuss E_v and E_d first, and the others later.

E_v *and* E_d

These energy terms can be calculated in terms of the respective force constants, which can be determined precisely by vibrational spectroscopies such as IR and Raman. Theoretically, the force constants can be estimated by computing the first derivatives of the energy gradients. At present, the calculation by the *ab initio* MO method within the Hartree-Fock level overestimates the diagonal elements of the force constant matrix by 10 to 20%, and hence a scale-down factor must be introduced to obtain quantitative agreement with experimental values.[38] For larger deformation in the bond-breaking and -forming processes, the harmonic oscillator approximation no longer holds.

Since some difficulty in convergence arises in the SCF process of the MO calculation for these processes, it is necessary to devise some extrapolation procedure, *e. g.* curve-fitting with Morse function.[39] Lifson[40] has demonstrated dramatic improvements in the precision of vibrational calculations by replacing quadratic function with the Morse curve for stretch potential, and perhaps this approach, which will eventually replace the rest of harmonic functions with the Morse type, appears to be a promising way for our purpose. Bartell discusses the introduction of the anharmonic part of Morse function into the MM scheme.[18] The transferability of the experimentally or theoretically determined force constants is obvious from the fact that the IR and Raman peaks, observed in certain *narrow* wavenumber ranges, have been widely used for group assignment.

E_{el}, E_{nb} *and* E_{rot}

These energy terms are basically two-center terms. As discussed above, there is no direct correspondence between energy terms in the MO and MM schemes. Thus, some bold assumptions on the correspondence should be employed to draw useful information from the MO scheme. For this purpose, the semiempirical MO scheme is more informative than the *ab initio* one, since it can tell, though qualitatively, the magnitudes of certain one- and two-center terms. One should be careful, however, not to step beyond drawing general trends and characteristics from the semiempirical MO results. Detailed discussions of each term are as follows.

The E_{el} term in the MM scheme is essentially the same as the E_{el} in the MO scheme, and can be calculated from the electron distribution under point-charge or multi-pole approximation. Since the transferability of the bond moment has been well established, the electron distribution derived empirically from the bond moments is generally of good quality. As Allinger *et al.* proposed,[41] a minor adjustment of thus obtained electron distribution can be made by solving the Del Re type local bond orbital secular equations. A more reliable electron distribution for a small molecule can be obtained by the *ab initio* MO method with the basis-set of double-zeta quality, plus polarization functions. For a large molecule or macromolecules, estimation based on the *ab initio* calculation of the small model molecule provides satisfactory results.[42]

Although the E_{nb} in the MM scheme is calculated by equations for the through-space interaction between the isolated spherical atoms, there is no *a priory* rationalization for ignoring the through-bond interaction for atom pairs separated by two or three bonds (*cf.* observation of NMR coupling between these atoms). If the through-bond interaction is to be considered, the 1,4-type can be implicitly included in E_{rot} or can be treated separately as a new term under the name of *indirectly bonded interaction,* or whatever appropriate name. The alternative is to re-define the E_{nb} as the energy for the interaction between the nonbonded atoms. This definition facilitates the comparison of the E_{nb} with the corresponding terms in the MO scheme, since the sum of E_{res} and E_{exc} for the nonbonded atom pair in the semiempirical MO method is the sum of the through-space and through-bond interactions.

We examined for representative molecules, though not many, the distance dependence of the sum of the E_{res} and E_{exc} for particular nonbonded atom pairs. The plots can be classified into two groups according to the number of intervening bonds: one for the 1,4-nonbonded atom pair and the others for the nonbonded atom pair separately by more than three bonds. Figure 1

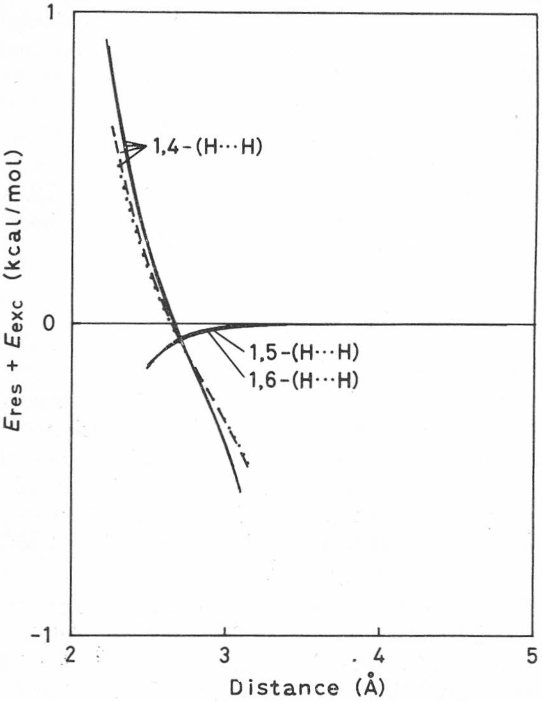

Figure 1. Distance dependence of the sum of resonance and exchange terms by the MNDO MO method for the 1,4-, 1,5-, and 1,6-nonbonded H···H pairs in *n*-butane and *n*-hexane (———), 1,2-dimethoxyethane (— — — — —) and 1,2-difluoroethane (···).[43]

is an example of such plots for H···H interactions in *n*-butane, 1,2-dimethoxyethane and 1,2-difluoroethane calculated by the MNDO method.[43] Similar results were obtained by the CNDO/2 and INDO methods.[43] The coincidence between the curves of the H···H interactions for non-polar *n*-butane and polar 1,2-difluoroethane suggests transferability of the thus determined E_{nb}, and also supports the conventional idea that the E_{nb} is the function of the pairing atom species and of the distance between them. The magnitude of the thus determined 1,4-E_{nb} is the largest for the H···H pair, but decreases for the more electronegative atom pair, the 1,4-E_{nb} contribution to conformational energies becoming noticeable when some of the hydrogens in the 1,4-positions are substituted by heteroatoms.

It should be noted that, irrespective of the pairing atom species, the 1,4-nonbonded interaction contributes to destabilization at *synclinal* positions and to stabilization at *antiperiplanar* positions due to the dihedral angle dependence of the bond order between 1,4-atoms.[44] Since the conclusion from the semiempirical MO calculation should be used only for qualitative purpose, the E_{nb} potential cannot be determined directly from the plots.[*6] Figure 1 clearly indicates that the introduction of a special E_{nb} function for the 1,4--nonbonded atom pair is necessary to improve the E_{nb} term in the MM scheme.

The E_{rot} in the MM scheme, defined for rotation about the 2—3 bond in the 1—2—3—4 atom sequence, is interpreted as the interaction between the 1—2 and 3—4 bonds in the localized MO scheme.[45] In the canonical MO scheme, which is usually referred to simply as the MO scheme, the concept of E_{rot} is not clear. Nor is the concept of E_{rot} in the MM scheme, and, nevertheless, the major part of conformational energy changes for rotamers comes from this uncertain term. In the semiempirical MO scheme, the ΣE_{rot} can be estimated by computing

$$\text{total energy} - \Sigma E_{\mathrm{el}} - \Sigma E_{\mathrm{nb}}$$

as a function of the dihedral angle. To compare this with the ΣE_{rot} in the MM scheme, the through-bond part of ΣE_{nb} should be added. The reduction of the thus determined ΣE_{rot} to certain 1—2—3—4 atom sequences, as is done in the MM scheme, is a matter of further discussion. One thing obvious at present from the semiempirical MO scheme is that ΣE_{rot}, and hence each component, is not of pure threefold symmetry. This is quite clear from the analysis of torsional energy curve of molecules lacking threefold symmetry in their internal rotational axis.

FINAL COMMENTS

The line of work as suggested above has a two-fold meaning. First, the knowledge of correspondence between MO and MM should serve to upgrade the MM scheme. In this case, the aim of MM will remain to reproduce experimental results with the best possible accuracy. An alternative development of MM is to reproduce the results of costly MO calculations. Though the first approach will continue to flourish for some time to come, the second approach has several attractive features. Above all, the *ab initio* based MM

[*6] The MNDO method gives quite satisfactory heats of formation (therefore the total energies). We found, however, that the ratio of energy components in Eq. 2 is not always reasonable. For example, about 50% of the total two-center energy for the 1—4 H···H nonbonded atom pair at cis position in *n*-butane is the E_{el} term.

will have the same flexibility as the *ab initio* MO, namely it should be able to parameterize for hetero atom systems as accurately as for hydrocarbons.

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REFERENCES AND NOTES

1. (a) *Molecular Mechanics,* U. Burkert and N. L. Allinger, Washington, D. C., American Chemical Society, 1982; (b) E. Ōsawa and H. Musso, *Angew. Chem. Int. Ed. Engl.* **22** (1983) 1; (c) A. Y. Meyer, *Molecular Mechanics and Conformation,* in: S. Patai and Z. Rappoport (Eds.), *The Chemistry of Functional Groups, Supplement D,* John Wiley & Sons, New York 1983, pp. 1; (d) *Aspekte von Kraftfeldrechnungen,* O. Ermer, München, Wolfgang Baur Verlag, 1981.
2. *Molecular and Crystal Structure Models,* A. Walton, Chichester, Ellis Horwood, 1978.
3. J. Weber, M. Roch, J.-J. Combremont, P. Vogel, and P.-A. Carrupt, *J. Mol. Struct.* **93** (1983) 189 and references cited therein.
4. *Quantum Pharmacology,* W. G. Richards, Second Edition, London, Butterworths, 1983, pp. 159.
5. (a) *Quantum Chemistry,* H. F. Schaefer, III, Oxford, Oxford University Press, 1984; (b) *New Horizons of Quantum Chemistry,* P. Löwdin, and B. Pullman (Eds.), Dordrecht, D. Reidel Publ. Co., 1983; (c) *Molecular Quantum Mechanics,* P. W. Atkins, Second Edition, Oxford, Oxford University Press, 1983.
6. Literature database: (a) K. Ohno and K. Morokuma, *J. Mol. Struct. Theochem* **8** (1982) 1; (b) *A Bibliography of Ab Initio Molecular Wave Functions: Supplement for 1978—80,* W. G. Richards, P. R. Scott, V. Sackwild, and S. A. Robins, New York, The Clarendon Press, 1981.
7. M. J. S. Dewar, *J. Mol. Struct.* **100** (1983) 41.
8. L. Schäfer, *J. Mol. Struct.* **100** (1983) 51.
9. J. P. Stewart, *QCPE Bull.* **3** (1983) 43.
10. (a) M. J. Wojcik, A. Y. Hirakawa, M. Tsuboi, S. Kato, and K. Morokuma, *Chem. Phys.* **100** (1983) 523; (b) Y. Hamada, K. Hashiguchi, A. Y. Hirakawa, M. Tsuboi, M. Nakata, M. Tasumi, S. Kato, and K. Morokum a, *J. Mol. Spectrosc.* **102** (1983) 123; (c) P. Pulay, G. Fogarasi, G. Pongor, J. E. Boggs, and A. Vargha, *J. Amer. Chem. Soc.* **105** (1983) 7037.
11. (a) D. Cremer, *J. Comput. Chem.* **3** (1982) 154, 165. (b) L. Schäfer, C. Van Alsenoy, and J. N. Scarsdale, *J. Mol. Struct.* **86** (1982) 349. (c) A. J. Thakkar, *J. Chem. Phys.* **79** (1983) 523. (d) K. B. Wiberg, *J. Comput. Chem.* **5** (1984) 197.
12. L. Radom *et al. J. Mol. Struct.* **126** (1985) 271.
13. See for example, K. Raghavachari, *J. Chem. Phys.* **81** (1984) 1383.
14. K. Kuchitsu and K. Oyanagi, *Faraday Discuss. Chem. Soc.* **62** (1977) 20.
15. C. D. Chalk, B. G. Hutley, J. McKenna, L. B. Sims, and I. H. Williams, *J. Amer. Chem. Soc* **103** (1981) 260 and the following papers of this series.
16. G. Giunchi and L. Barino, *Gazz. Chim. Ital.* **110** (1980) 407.
17. L. S. Bartell, S. Fitzwater, and W. J. Hehre, *J. Chem. Phys.* **63** (1975) 4750.
18. (a) S. Fitzwater and L. S. Bartell, *J. Amer. Chem. Soc.* **98** (1976) 5107; (b) L. S. Bartell, *Ibid.* **99** (1977) 3279; (c) L. S. Bartell, S. Fitzwater, and W. J. Hehre, *J. Chem. Phys.* **63** (1975) 3042.
19. (a) G. A. Jeffrey and R. Taylor, *J. Comput. Chem.* **1** (1980) 99; (b) S. J. Weiner, P. A. Kollman, D. A. Case, U. C. Singh, C. Ghio, G. Alagona, S. Profeta, Jr., and P. Weiner, *J. Amer. Chem. Soc.* **106** (1984) 765; (c) N. L. Allinger, U. Burkert, and S. Profeta, Jr. *J. Comput. Chem.* **1** (1980) 281; (d) *Conformational Analysis of Aliphatic Amines by Force Field and Quantum Mechanical Methods,* S. Profeta, Jr., Athens,

Georgia, University of Georgia, 1978; (e) C. Jaime and E. Ōsawa, *Tetrahedron* **39** (1983) 2769.

20. (a) F. A. Van-Catledge and N. L. Allinger, *J. Amer. Chem. Soc.* **104** (1982) 6272; (b) L. Schäfer, C. Van Alsenoy, and J. N. Scarsdale, *J. Mol. Struct.* **86** (1982) 349; (c) N. L. Allinger and S. Profeta, Jr. *J. Comput. Chem.* **1** (1980) 181; (d) N. L. Allinger, J. Kao, H.-M. Chang, and D. B. Boyd, *Tetrahedron* **32** (1976) 2867; (e) D. A. Dougherty and K. Mislow, *J. Amer. Chem. Soc.* **101** (1979) 1401.
21. (a) N. L. Allinger and J. T. Sprague, *J. Amer. Chem Soc.* **95** (1973) 3893; (b) J. Kao and N. L. Allinger, *Ibid.* **99** (1977) 975; (c) K. B. Lipkowitz, A. M. Naylor, and W. B. Melchior, *Tetrahedron Lett.* **25** (1984) 2297; (d) S. Lifson, C. E. Felder, and A. Shanzer, *J. Amer. Chem. Soc.* **105** (1983) 3866; (e) A. Warshel and N. Barboy, *Ibid.* **104** (1982) 1469; (f) A. Warshel and A. Lappicirella, *Ibid.* **103** (1981) 4664; (g) J. B. M. Somers, J. H. Borkent, and W. H. Laarhover, *Rec. Trav. Chim. Pays-Bas* **100** (1981) 110; (h) W. Paulick, Ch. Jung, U. Kempka, J. Sühnel, and K. Gustav, *J. Mol. Struct.* **85** (1981) 235; (i) J. Sühnel, U. Kempka, and K. Gustav, *J. Prakt. Chem.* **322** (1980) 649; (j) A. Warshel, *The Consistent Force Field and Its Quantum Mechanical Extension,* in: G. Segal (Ed.), *Modern Theoretical Chemistry,* Vol. 7, Plenum, New York 1977, pp. 133—172.
22. (a) E. Ōsawa, E. M. Engler, S. A. Godleski, P. v. R. Schleyer, Y. Inamoto, and G. J. Kent, *J. Org. Chem.* **45** (1980) 984; (b) E. Ōsawa, Y. Onuki, and K. Mislow, *J. Amer Chem. Soc.* **103** (1981) 7475; (c) W. D. Hounshell, D. A. Dougherty, J. P. Hummel, and K. Mislow, *Ibid.* **99** (1977) 1916; (d) R. Yamaguchi, M. Ban, M. Kawanisi, E. Ōsawa, C. Jaime, A. B. Buda, and S. Katsumata, *J. Amer. Chem. Soc.* **106** (1984) 1512; (e) J. Kao and L. Radom, *Tetrahedron* **34** (1978) 2515; (f) D. A. Dougherty, H. B. Schlegel, and K. Mislow, *Tetrahedron* **34** (1978) 1441; (g) K. Harano, T. Ban, M. Yasuda, E. Ōsawa, and K. Kanematsu, *J. Amer. Chem. Soc.* **103** (1981) 2310; (h) E. Ōsawa, P. M. Ivanov, and C. Jaime, *J. Org. Chem.* **48** (1983) 3990; (i) K. Okamoto, K. Kanematsu, T. Fujiyoshi, and E. Ōsawa, *Tetrahedron Lett.* **24** (1983) 5645.
23. K. Ohno, H. Mutoh, and Y. Harada, *J. Amer. Chem. Soc.* **105** (1983) 4555.
24. T. Hirano, T. Miyajima, K. Kato, and H. Sato, *J. Chem. Soc., Chem. Commun.* (1984) 935.
25. The MP2 electron correlation calculations with 6-311G** basis set can reproduce only ca. one third of the observed gauche-preference: T. Hirano, Y. Kurita, and T. Miyajima, *Preprints for the* **49***th Annual Meeting of the Chemical Society of Japan,* Apr. 1984, p. 36.
26. J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Seeger, D. J. DeFrees, H. B. Schlegel, S. Topiol, L. R. Kahn, and J. A. Pople, *QCPE* **13** (1981) 406, 437.
27. Decomposition of the Hartree-Fock molecular energy into one-, two-, three- and four-center energies (bond energy analysis) is reported by E. Clementi, *J. Chem. Phys.* **46** (1967) 3842; *Int. J. Quantum Chem. Symp.* **3** (1969) 179.
28. E. Clementi and W. von Niessen, *J. Chem. Phys.* **54** (1971) 521.
29. T. Hirano, *Kobunshi /High Polymers, Japan* **30** (1981) 102.
30. J. A. Pople and G. A. Segal, *J. Chem. Phys.* **44** (1966) 3289.
31. J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.* **47** (1967) 2026.
32. N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.* **50** (1969) 1262; N. C. Baird, M. J. S. Dewar, and R. Sustmann, *Ibid.* **50** (1969) 1275.
33. M. J. S. Dewar, and E. Haselbach, *J. Amer. Chem. Soc.* **92** (1970) 590; N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *Ibid.* **92** (1970) 3854.
34. R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.* **97** (1975) 1285.
35. M. J. S. Dewar and W. Thiel, *J. Amer. Chem. Soc.* **99** (1977) 4899.
36. J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.* **43** (1965) S129.
37. For the INDO and MNDO MO's, T. Hirano, unpublished results.

38. *Ab Initio Calculations, Lecture Notes in Chemistry Vol. 16,* P. Čársky and M. Urban, Berlin, Springer, 1980, pp. 144.
39. S. Watanabe, T. Hirano, K. Sato, H. Natsuaki, K. Fueki, and H. Koinuma, *Preprints for the 48th Annual Meeting of the Chem. Soc. Japan* Aug. 1983, p. 148.
40. A. T. Hagler, P. S. Stern, S. Lifson, and S. Ariel, *J. Amer. Chem. Soc.* **101** (1979) 813.
41. L. Došen-Mićović, D. Jeremić, and N. L. Allinger, *J. Amer. Chem. Soc.* **105** (1983) 1716, 1723.
42. *Cf.* V. Sackwild and W. G. Richards, *J. Mol. Struct. Theochem* **6** (1982) 269.
43. T. Miyajima, K. Kato, and T. Hirano, *Preprints for the 48th Annual Meeting of the Chem. Soc. Japan* Aug. 1983, p. 520.
44. T. Hirano, in: W. J. Bailey, and T. Tsuruta (Eds.), *Contemporary Topics in Polymer Science,* Vol. 4, Plenum Press, New York, 1984, pp. 545—550.
45. T. K. Brunck and F. Weinhold, *J. Amer. Chem. Soc.* **101** (1979) 1700.

SAŽETAK

O povezanosti energija molekulskih orbitala i članova empirijskoga potencijalnog polja

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Da bi se izbjegle teškoće empirijske parametrizacije potencijalnih funkcija za heteroatome u molekulskoj mehanici (MM), predloženo je da se uporabe neke teorijske *ab initio* veličine. U tu svrhu analizirana je korespondencija između pojedinih članova MM-potencijalne energije i MO veličina. Interakcije koje dovode do istezanja veza, savijanja kutova, a i elektrostatsko međudjelovanje naboja, mogu se bez većih teškoća izračunati s pomoću MO metoda. Istaknuto je da MM sheme ne uključuju nevezne interakcije na zadovoljavajući način, što posebno vrijedi za one 1,4-tipa. Razmatrana je mogućnost uklanjanja ovog nedostaka.