NEW PROGRAMS

Improved AMYR program: An algorithm for the theoretical simulation of molecular associations, including geometrical and topological characterization of the dimers

Francisco Torrens, Enrique Ortí, and José Sánchez-Marín

Departament de Química Física, Facultat de Química, Universitat de València, Dr. Moliner 50, E-46100 Burjassot, València, Spain

Program AMYR, originally written by S. Fraga (University of Alberta, Canada), allows for the calculation of molecular associations using a pair-wise atom–atom potential. The interaction energy is evaluated through a 1/R expansion. Our improved version includes a dispersion energy term in the potential corrected by damping functions, the possibility of carrying out energy minimizations through variable metric methods, as well as the optional calculation of geometrical and topological indices. Program AMYR has been adapted also for high-performance computing and vectorization. An interactive version of the program carries out real-time molecular graphics showing simultaneously the energy profile of the calculations.

Keywords: molecular associations, pair potential, 1/R expansion, geometry optimization, vectorization, molecular graphics

Address reprint requests to Dr. Torrens at the Departament de Química Física, Facultat de Química, Universitat de València, Dr. Moliner 50, E-46100 Burjassot, València, Spain.
Received 26 February 1991; accepted 12 March 1991

INTRODUCTION

Program AMYR for the theoretical simulation of molecular associations determines the optimum separation and relative orientation of two interacting molecular systems through a minimization of the interaction energy.[1,2] The interaction energy is evaluated by means of a $1/R$ expansion.[1–4] The initial position of the second system with respect to the first one is defined by means of a sixfold vector (three translations and three rotations) about the Cartesian axes. Because the number of atom–atom intermolecular interactions is formally proportional to the square of the number of atoms in the molecules, a great incentive exists to incorporate vectorization into the AMYR algorithm.[5,6]

DESCRIPTION

The association energy is evaluated by means of the atom–atom pair potential proposed by S. Fraga:[1,2]

$$E_{ij} = 1389.4168 q_i q_j / R_{ij} - 694.70838 (f_i \alpha_i q_j^2 + f_j \alpha_j q_i^2)/R_{ij}^4 - 1516.0732 f_i \alpha_i f_j \alpha_j / [(f_i \alpha_i / n_i)^{1/2} + f_j \alpha_j / n_j)^{1/2}] R_{ij}^6 + 4.184 c_i c_j / R_{ij}^{12} \quad (1)$$

where q is the net atomic charge; $n = Z - q$ is the total atomic charge; α is the atomic polarizability; and f and c are parameters that were adjusted to reproduce accurate SCF results.[1] The total interaction energy between molecules A and B is the double sum of E_{ij} over every atom i of molecule A and every atom j of molecule B. The present version includes parameters for several atoms, most of which (H, Li, C, N, O, Na, S, K, and Ca) can be assigned to 82 classes for which coefficients are available.[1–4] The following improvements have been implemented in the AMYR program:[5,6]

(1) Long-range term. The program performs an initial assignment of net atomic charges. A renormalization of these net charges is followed to reproduce the required total molecular charge. A further renormalization is carried out to reproduce the first nonzero multipole moment.
(2) Medium-range term. AMYR algorithm carries out an interpolation of the atomic polarizabilities

as a function of the renormalized net charges. The medium- and short-range terms related with the atomic polarizabilities can be corrected by means of a damping function proposed by Douketis *et al.*[7]

(3) Short-range term. The program allows us to include a dispersion energy term by means of an additional $1/R^6$ term in the potential with either the Slater-Kirkwood or Mulder formulas. The Slater-Kirkwood formula uses a term equal to the $1/R^6$ term of Fraga (Equation (1)) but where the factors f are now set equal to 1. Mulder's formula requires an additional energy term of the form:

$$E_{ij} = -57.65056465 D_{ij}/R_{ij}^6 \quad (2)$$

(4) Optimization of the intermolecular energy. The search for the minimum energy can be carried out by one of the following options: nonderivative simplex method, derivative steepest-descent, Davidon and Broyden-Fletcher-Goldfarb-Shanno (BFGS) optimization methods. The BFGS procedure is recommended as a fast standard method.

(5) Adaptation for the calculation of geometrical and topological magnitudes. Molecular volume, bare molecular surface area and topological indices (molecular globularity and molecular congestion) are calculated with a numerical method proposed by Meyer.[8] The underlying conceptual model represents atoms as spheres and molecules as systems of overlapping spheres. The solvent accessible surface is defined and the corresponding area is calculated by the method of the probe sphere proposed by Lee and Richards.[9]

(6) Adaptation for the realization of high-performance computing and vectorization. The program has been implemented in an IBM-3090 vector facility. Program AMYR performs an exhaustive use of calls to the IBM Engineering and Scientific Subroutine Library (ESSL) that has been used whenever possible. The rest of the code has been rewritten for the vector facility by programming efficient algorithms in VS Fortran.

(7) Adaptation for the performance of interactive calculations with the realization of real-time molecular graphics. A molecular graphics routine library called GRAPHLIB has been prepared for interactive calculations.

APPLICATION

The improved AMYR program[5,6] has been fully tested by us. Benzene and azine dimers,[10–12] phthalocyanine dimers,[13] and clusters[14] and coronene aggregates[15] have been calculated. Figure 1 shows the energy profile through the *XY*-bisector for the slipping displacement of the face-to-face stacked structure corresponding to the phthalocyanine dimer.[13] A grid scan of 30 sets has been performed and molecule *B* has been represented for both sets 1 and 30. Center-of-mass coordinates varies from $(X,Y,Z) = (0,0,3.17)$ Å (set 1) to (14.5,14.5,3.17) Å (set 30) with a step of 0.5 Å in both *X*- and *Y*-axes. Set 1 corresponds to a maximum of +18.7 kJ/mol and set 12 corresponds to a minimum of −229 kJ/mol. The energy tends to 0 in the limit of long distances.

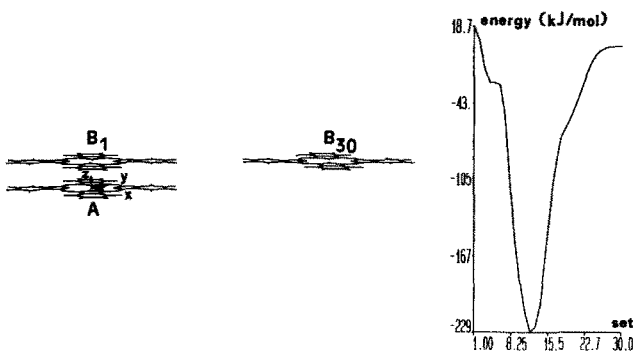

Figure 1. Energy profile of the phthalocyanine dimer for a slipping displacement through the XY*-bisector (corresponding to sets 1 to 30)*

CONCLUDING REMARKS

A high-performance version of program AMYR has been adapted for an IBM 3090-150E-VF (VM/CMS) with the VS FORTRAN compiler 2.4 and ESSL library rel. 4. A real-time molecular graphics version has been implemented in a DIGITAL VAX-8300 (VMS) with the VAX FORTRAN Compiler 5.4 and VAX GKS/0b 1.0. Both versions are available via EARN/BITNET 'TORRENS@EVALUN11.EARN', and are discussed in detail in a recent publication.[6]

ACKNOWLEDGEMENTS

We acknowledge Dr. S. Fraga for providing us with an early version of AMYR as well as any required information and documentation about it. This work has been supported by the project PS88-0112 of the spanish DGICYT. This research has been preformed using the resources of the Servei d'Informàtica de la Universitat de València.

REFERENCES

1 Fraga, S. A semiempirical formulation for the study of molecular interactions. *J. Comp. Chem.* (1982) **3**, 329–334

2 Fraga, S. Molecular associations. *Comp. Phys. Commun.* (1983) **29**, 351–359

3 Nilar, S.H.M. and Fraga, S. Molecular associations: Values of the expansion parameters for new classes of atoms. *J. Comp. Chem.* (1984) **5**, 261–262

4 Sordo, J.A. and Fraga, S. Molecular associations: Values of the expansion parameters for new classes of atoms. *J. Comp. Chem.* (1986) **7**, 55–57

5 Torrens, F., Montañana, R. and Sánchez-Marín, J. Vectorizing pair-potential AMYR program for the study of molecular associations. In: *High-Performance Computing*. (J.-L. Delhaye and E. Gelenbe, Eds.) North-Holland, Amsterdam, 1989, 299–308

6 Torrens, F., Ortí, E. and Sánchez-Marín, J. Pair-potential calculation

of molecular associations: A vectorized version. *Comp. Phys. Commun.* accepted
7 Douketis, C., Scoles, G., Marchetti, S., Zen, M. and Thakkar, A.J. Intermolecular forces via hybrid Hartree-Fock-SCF plus damped dispersion (HFD) energy calculations: An improved spherical model. *J. Chem. Phys.* (1982) **76**, 3057–3063
8 Meyer, A.Y. Molecular mechanics and molecular shape V: On the computation of the bare surface area of molecules. *J. Comp. Chem.* (1988) **9**, 18–24
9 Lee, B. and Richards, F.M. The interpretation of protein structures: Estimation of static accessibility. *J. Mol. Biol.* (1971) **55**, 379–400
10 Torrens, F., Sánchez-Marín, J., Ortí, E. and Nebot-Gil, I. Incorporation of a dispersion energy term to Fraga's atom–atom pair intermolecular potential: Application to benzene, *s*-tetrazine and their mixed dimers. *J. Chem. Soc. Perkin Trans. 2* (1987), 943–950
11 Torrens, F., Sánchez de Merás, A.M. and Sánchez-Marín, J. The use of *ab initio* net charges to improve Fraga's atom–atom pair potential for molecular association. *J. Mol. Struct. (Theochem)* (1988) **166**, 135–140
12 Torrens, F., Sánchez-Marín, J. and Tomás, F. Intermolecular calculations on azine dimers. *J. Chem. Res. (S)* (1990), 176–177
13 Torrens, F., Ortí, E. and Sánchez-Marín, J. Structural and charge effects on the phthalocyanine dimer. In: *Modeling of Molecular Structures and Properties*. (J.-L. Rivail, Ed.) North-Holland, Amsterdam, 1990, 221–228
14 Torrens, F., Ortí, E., and Sánchez-Marín, J. Electrically conductive phthalocyanine assemblies. Structural and noninteger oxidation number considerations. In: *Lower-Dimensional Systems and Molecular Devices*. (R.M. Metzger, P. Day and G.C. Papavassiliou, Eds.) Plenum, New York, 1991, 481–488
15 Rodríguez, J., Sánchez-Marín, J., Torrens, F. and Ruette, F. Molecular aggregation of polycyclic aromatic hydrocarbons: A theoretical modeling of coronene aggregation. *J. Mol. Struct. (Theochem)*, accepted