



# Hybrid Molecular Mechanics: For Effective Crystal Field Method for Modeling Potential Energy Surfaces of Transition Metal Complexes

M. B. DARHOVSKII<sup>-2</sup> M. G. RAZUMOV<sup>3</sup> I. V. PLETNEV,<sup>2,4</sup>  
A. L. TCHOUGREEFF<sup>12</sup>

<sup>1</sup>*L. Y. Karpov Institute of Physical Chemistry, Moscow, Russia*

<sup>2</sup>*Center for Computational Chemistry at the M. V. Keldysh Institute/or Applied Mathematics of RAS, Moscow, Russia*

<sup>3</sup>*N. S. Kurnakov Institute of General and Inorganic Chemistry of RAS, Moscow, Russia*

<sup>4</sup>*Kemistry Department, M. V. Lomonosov Moscow State University, Moscow, Russia*

Received 20 July 2001; accepted 22 December 2001

Published online 14 May 2002 in WUey InterScience (www.interscience.wiley.com).

DOI 10.1002/cjua.10211

**ABSTRACT:** The effective crystal field (ECF) methodology previously developed for description of the electronic structure of transition metal complexes (TMCs) is combined with molecular mechanics (MM) formalism. In this way, a new method for calculations of potential energy surfaces of the Werner-type TMC is developed. It is based on a combined quantum mechanics (QM)-MM approach with the ECF method taking part of the QM and advanced MM package MMPC developed for the metal ion complex computations and based on the CHARMM organic force field. The MM region consists of ligand atoms and metal ion coordination sphere, leaving out effects of d-shell, while the QM region is limited to metal ion d-shell. Crystal field matrix for the d-shell is calculated with use of the local ECF method. It is shown that the procedure proposed reproduces with considerable accuracy geometry characteristics of values of the Fe(II) complexes with both mono- and polydentate ligands. © 2002 Wiley Periodicals, Inc. *Int J Quantum Chem* 88: 588-605, 2002

**Key words:** effective crystal field; transition metal complexes; potential energy surfaces; quantum mechanics/molecular mechanics

## Introduction

Molecular mechanics (MM) [1] is widely used in calculations of potential energy surfaces (PESs) of organic molecules, both *per se* and in

molecular dynamics simulations. The conventional MM scheme faces, however, significant problems when applied to the metal ion complexes. The main problem is an adequate modeling of coordination sphere, which, in fact, presents two closely related subproblems: accounting for coordination polyhedron flexibility and for electronic structure details.

Conventional MM considers metal center (as well as all the other atoms) as having a definite

Correspondence to: A. L. Tchougrëff; e-mail: andrei@cc.nifhi.ac.ru.