化学学报 2005 63 (6): 465-472 ISSN: 0567-7351 CN: 31-1320/06

研究论文

过渡金属体系非线性光学性质计算的ECP基组研究

刘彩萍，吴克琛*，洪涛，莽朝永，张明昕，韦永勤，周张锋，庄伯涛

(中国科学院福建物质结构研究所结构化学国家重点实验室 福州 350002)

收稿日期 2004-6-7 修回日期 2004-11-29 网络版发布日期 接受日期

摘要 有效核势(ECP)方法是计算含有过渡金属体系的电子结构及物理性质的有效方法.
本文比较了一系列典型的ECP基组对计算含过渡金属体系非线性光学性质精度的影响. 分别在HF, MP2和DFT理论水平上对过渡金属元素使用不同的ECP基组, 计算了几个过渡金属有机化合物的静态一阶超极化率β_0.
研究结果表明: 使用有效核势计算含过渡金属体系时, 核电子的选取是提高计算精度的前提, *n*s和*n*p电子应该和*n*d电子一同作为价电子处理; 对于重原子, 必须考虑自旋-轨道耦合相对论效应. 经过综合评估, 认为使用Stuttgart/Dresden赝势的ECP基组, MHF, 在计算含有过渡金属体系非线性光学性质方面是比较好的基组; Stuttgart RSC 1997和SBKJC VDZ相对而言是较好的基组; 基组Lanl2dz, Hay-Wadt MB (*n*－1)和Hay-Wadt VDZ (*n*－1)由于没有考虑自旋-轨道耦合, 计算精确度次之; 而基组CRENBL和CRENBS计算的偏差要大一些, 尤其是CRENBS基组由于价电子选择得太少而导致与实验值的偏差最大.

关键词 从头计算 ECP基组 过渡金属有机化合物 静态一阶超极化率

分类号

Study on ECP Basis Sets for Calculating Nonlinear Optical Properties of Transition Metal Systems

LIU Cai-Ping, WU Ke-Chen*, HONG Tao, MANG Chao-Yong, ZHANG Ming-Xin, WEI Yong-Qin, ZHOU Zhang-Feng, ZHUANG Bo-Tao

(*State Key Laboratory of Structural Chemistry, Fujian Institute of the Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002*)

Abstract The effective core potential (ECP) approach provides a successful way to calculate the electronic structures of transition metal systems. The performance of several typical ECP basis sets on calculating the nonlinear optical properties of transition metal systems has been evaluated. The static first hyperpolarizabilities β_0 of some typical organometallic compounds have been studied at the HF, MP2 and DFT levels by using different ECP basis sets for metallic atoms. To calculate properties of transition metal systems accurately, the electrons of *n*s and *n*p orbitals should act as valence electrons as well as those of *n*d. Alternatively speaking, the effect of spin-orbit-coupling is uppermost in relativistic effects. By comparison, the ECP basis set, MHF, was good for computing the first hyperpolarizabilities of organometallic systems, and the Stuttgart RSC 1997 and the SBKJC VDZ were relatively good. The Lanl2dz, the Hay-Wadt MB (*n*－1) and the Hay-Wadt VDZ (*n*－1) did not apply the spin-orbit-coupling, so their calculating accuracy was a little poorish. Whereas the CRENBL and the CRENBS provided larger deviations between the computed and experimental values than other ECP basis sets.

Key words *ab initio* ECP basis set transition metal organometallic compound the static first hyperpolarizability

DOI:

通讯作者 吴克琛 wkc@ms.fjirsm.ac.cn