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遷移元素におけるスピン軌道相互作用定数について

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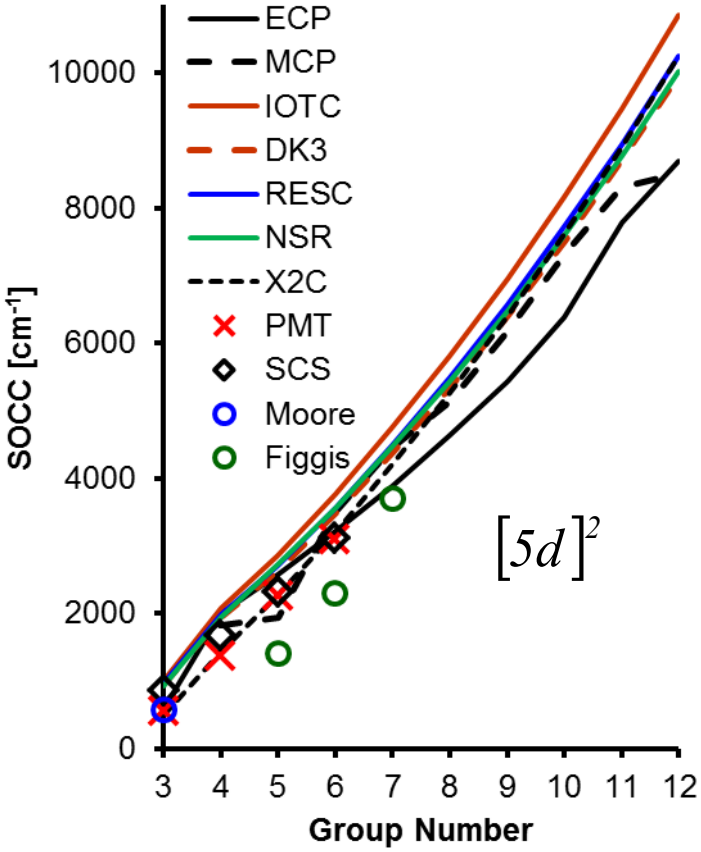
The spin-orbit coupling constants (SOCCs) were calculated for the low-lying atomic states whose main configuration is $[nd]^q$, q = 1 ~ 9 and n being the principal quantum number, in the first- through third-row transition elements and their ions by using four different computational relativistic methods, effective core potential (ECP), model core potential (MCP), all-electron (AE), and exact two-component (X2C) transformation. The first three methods are so-called two-step approach (TSA), while the last method X2C is a one-step approach (OSA). In the AE method, three different calculations, relativistic elimination of small components (RESC), third-order Douglas-Kroll (DK3) transformation, and infinite-order two-component (IOTC) relativistic correction, were performed for the estimation of the scalar relativistic parts in addition to nonscalar relativistic (NSR) calculations. The calculated SOCCs were compared with the available experimental data. Although there are several exceptions including the states whose main configuration is $[nd]^5$, the averaged differences between the calculated ECP and AE (IOTC) SOCCs and between the calculated ECP and the X2C SOCCs are mostly less than 20%. The differences between the calculated ECP and experimental SOCCs are even smaller. No serious discrepancy was found between the TSA and OSA predictions of SOCCs for the first- and second-row elements. For the third-row elements and their ions, the SOCCs are not always good indicators for the discussion of relativistic effects because of the magnitude of the spin-orbit coupling (SOC). The LS coupling scheme is inappropriate and the jj coupling scheme should be used in such strong field. For more useful discussion of relativistic effects, it is necessary to examine how electronic states split into spin-mixed (SM) states. According to the present analyses of the splittings of the SM states, it is found that the ECP results get comparable results to those obtained by X2C (OSA). Thus, it is anticipated that the analyses using the ECP methods are applicable to relativistic investigations of molecular systems and/or heavy metal complexes.



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