Comment on "going beyond the frozen core approximation: Development of coordinate-dependent pseudopotentials and application to Na2 +" [J. Chem. Phys. 138, 054110 (2013)]

Stoll, Hermann

Fuentealba, Patricio

Von Szentpály, László

The new coordinate-dependent pseudopotential for Na2 + by Kahros and Schwartz J. Chem. Phys. 138, 054110 (2013) is assessed and compared to the pseudopotential approach by Fuentealba Chem. Phys. Lett. 89, 418 (1982) which incorporates the coordinate-dependent core-polarization potential by Müller and Meyer J. Chem. Phys. 80, 3311 (1984). In contrast to the latter approach, the one by Kahros and Schwartz does not reproduce the accurately known experimental data and/or high level theoretical results for Na2 +. The treatment of core polarization by Kahros and Schwartz neglects the dynamic polarization of atomic cores which is much more important for Na2 + than the static one. On the other hand, the Kahros and Schwartz method heavily overestimates frozen-core corrections at the Hartree-Fock level by compounding them with artifacts of a superposition of non-norm-conserving pseudopotentials.