CRITERIA OF PARAMETER SELECTION FOR QUANTUM CHEMICAL SIMULATION OF THE ELECTRONIC STRUCTURE OF RARE-EARTH IONS BY THE SCATTERED WAVE CLUSTER METHOD

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Electronic structure calculations of the Ce\(^{3+}\) ion in terms of a molecular cluster model in a quasirelativistic approximation are reported. The influence of the self-interaction correction and variations of muffin-tin parameters on the calculation results is discussed. A method is proposed for estimating the 4f\(\rightarrow\)5d transition energy in the cerium ion using the SCF–SW formalism.

INTRODUCTION

The ions of rare-earth elements (REE) are activators in a number of chemical compounds with a complex crystal structure. Many REE-containing dielectrics are known to be efficient scintillators and have gained widespread acceptance as solid state ionizing radiation detectors [1]. Theoretical analysis of the electronic structure of these compounds provides additional information for understanding the mechanisms of luminescence in a great number of REE-activated systems.

In electronic structure calculations of low-symmetry quantum chemical systems, the cluster methods are most convenient since they are relatively simple and allow a description of both ideal and defective crystals in terms of a single approach. At the same time, the routinely used cluster models based on the self-consistent field scattered wave (SCF–SW) method [2] employ the muffin-tin (MT) and density functional approximations as well as relativistic effect and boundary condition corrections. The spectrum is affected by these approximations in different ways depending on the structure of the electronic shells of the ion, which makes the calculation results uncertain. Therefore, determining the order of the errors introduced into calculations by each approximation, that is, establishing the strict hierarchy of approximations for each type of physical and chemical problem is essential for computational solid state physics. This problem is of particular importance for REE ions because of the specific features (shape, extent, fast oscillation) of the f-electron wave functions. The aim of this work is to determine the order of errors in scattered wave cluster calculations of the electronic structure of the ions of 4f elements using Ce\(^{3+}\) as an example. The effects of the MT approximation parameters and of the local shape of the exchange correlation potential as well as the influence of relativistic effects are analyzed.

CALCULATION PARAMETERS

We investigated the influence of the muffin-tin approximation parameters on the one-electron energy spectrum of the cluster model of REE. From general analysis it follows that, irrespective of the criteria for choosing the MT sphere radii, the potential and electron density will have discontinuities of first kind at the boundaries of the MT spheres of the cluster ions. The effect of these discontinuities on the spectrum can be estimated by comparing the results of molecular cluster modeling for the ion with the results of calculations (using Desclaux type programs [3]) for an isolated ion for which the potential is a continuous spherically symmetric function of the radius vector modulus. The boundary conditions are evidently not imposed. The cluster is a molecule composed of the central sphere incorporating the ion core and of

several empty spheres (vacancies — V) on the periphery of the cluster. Here "vacancy" is a conventional term which does not mean the absence of any ion in the cluster. As shown by calculations, the type of arrangement (octahedral, tetrahedral, or chaotic) of empty spheres is not relevant to the result. The essential parameters are the radii of the spheres and the distances to the center of the cluster. The ion—empty sphere approximation allows one to regard the results of cluster calculations as pseudoatomic (ionic) and to compare our data with the data for isolated ions.

Self-consistent molecular calculations including relativistic corrections were carried out for the [CeV₆]³⁺ cluster of Oh symmetry. The self-consistency procedure was performed for the 5d and 4f states (other states were considered "frozen"); core densities were calculated using the relativistic version of the Desclaux program, with the 5d state corresponding to the molecular orbitals e₈ and t₂g, and the 4f state corresponding to t₁u, t₂g, and e₂u. Partial wave expansion was employed: lₓₐₓ(Ce) = 3, lₓₐₓ(V) = 2, lₓₐₓ(SW) = 3. For comparison with atomic calculations, below we give the energies of the centers of gravity for the corresponding molecular states. The local exchange correlation potential in the Vosko–Wilk–Nusair [4] parameterization was used. The calculations were made for configurations with vacant 5d and 4f states (4f¹5d⁰ and 4f⁰5d¹ configurations, respectively), and for the Slater transition state [5] (4f⁰5d⁰5f⁰ configuration).

The MT spheres were contacting; the calculations were performed for three vacancy radii (Rᵥ): 0.5, 0.7, and 0.9 Å. The MT ionic radii of cerium (Rₑ) were varied from 1.2 to 1.5 Å. By virtue of contacting spheres, the variations in Rₑ are related to changes in the interionic distance Ce—V.

CALCULATION OF RELATIVISTIC CORRECTIONS

A characteristic feature of REE-containing coordination compounds is the presence of d and f electrons. This alters the requirements to the calculation techniques used for electronic structure determination of such systems. In this case, we have a considerable contribution of relativistic effects, which are usually ignored in solving the nonrelativistic Schrödinger equation. For example, for the trivalent cerium ion [6], the relativistic shift of the 4f energy level is 2.3 to 3 eV. For relativistic effect calculation, the quantum chemical approach should then be based on the relativistic Hamiltonian and the Dirac relativistic four-component wave functions. For cluster models, this approach involves bulky equations [6], which are very difficult or sometimes impossible to solve in the absence of appropriate computer facilities. Fortunately, chemical bonding mostly involves outer electrons, for which the so-called quasirelativistic approximation (QRA) [7] is quite acceptable. The use of QRA allows a relatively simple solution of the problem in terms of the pseudopotential approach. In this case, the problem can be reduced to solution of the standard wave equation with relativistic corrections calculated during the construction of the potential.

QRA uses three types of correction:
1) for velocity dependence of electron mass;
2) for Darwin’s interaction;
3) for spin-orbital interaction.

The first two corrections do not affect the symmetry of the nonrelativistic Hamiltonian, while the spin-orbital interaction correction contains operators for both coordinate and spin space decreasing the symmetry of the problem. Hence, the optimal way of introducing QRA into the SCF–SW scheme is adding relativistic corrections not affecting the symmetry of the problem to the self-consistent procedure. The mass—velocity and Darwin corrections are directly introduced into the potential construction scheme within the MT sphere of the REE ion [7]. The spin-orbital interaction correction may be applied in the final step, after self-consistent one-electron levels for valence electrons have been obtained using the first-order perturbation theory approximation.

RESULTS AND DISCUSSION

Figure 1 shows the calculation results for the molecular cluster [CeV₆]³⁺ simulating the Ce³⁺ ion for different configurations and Ce³⁺—empty sphere distances. The results reflect the influence of the geometrical parameters of the cluster directly related to the error of the MT approximation to the potential. The data are given in absolute units taking into account the position of the MT zero level relative to vacuum.

In nonrelativistic calculations (see Fig. 1a) for different values of Rᵥ for the 4f¹5d⁰ configuration, the energy of the 4f level (E₄f) is shifted insignificantly (0.3-0.4 eV) over the whole range of MT cerium radii, being approximately 31.32 eV. This value is in reasonable agreement with the result of the nonrelativistic atomic calculations for the Ce³⁺ ion.