# Brief Reports

## Treatment of semicore states in the linearized augmented-plane-wave method and other linearized electronic-structure methods

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We show that elements with semicore states can be treated by standard linearized methods if the radius of the muffin-tin sphere is chosen smaller than in standard implementations and if appropriate radial basis functions are used.

## I. INTRODUCTION

It is well known that linearized methods[1,2] give poor or even wrong results for elements with semicore states. Semicore states are extended core states that are not entirely contained in the muffin-tin sphere. Because the overlap between a radial valence wave function $R_v$ with eigenvalue $E_v$ and a radial core wave function $R_c$ with eigenvalue $E_c$ in the muffin-tin sphere of radius $r_c$ is given by

$$\int_0^{r_c} R_v R_c r^2 dr = \frac{1}{2} r_c^2 \frac{R_c \frac{\partial R_v}{\partial r} - R_v \frac{\partial R_c}{\partial r}}{E_c - E_v} \Bigg|_{r=r_c} ,$$

the orthogonality of the valence and core states can be violated if there are semicore states which leak out of the muffin-tin sphere. The only way to avoid the breakdown of the orthogonality is to include these semicore states as valence states.

Singh[3,4] recently proposed two ways to do this. In his first proposal he includes, in addition to the usual $u_l$ and $\dot{u}_l$ radial basis functions at the valence reference energy, the same set of functions at a semicore reference energy. The expansion coefficients of these four basis functions are determined by matching the value and the first three radial derivatives of each $l,m$ component at the surface of the sphere. Because the plane-wave expansion of the interstitial region must now also converge to the correct second and third derivatives on the surface of the muffin-tin sphere, more plane waves are required to satisfy these additional requirements and the plane-wave energy cutoff goes up.

His second proposal does not suffer from this disadvantage. As an additional radial basis function in the muffin-tin sphere he includes a function that has zero value and slope on the surface of the sphere and therefore does not directly couple to the plane waves. Because the

expansion coefficient of this third function is not determined by the plane waves, one has, in addition to the plane-wave expansion coefficients $c_K$, additional variational coefficients, which make programming somewhat more difficult.

We will now show that the standard linearized augmented-plane-wave (LAPW) method with only two radial functions gives accurate results for atoms containing semicore states if the muffin-tin sphere is smaller than usual and if appropriate radial basis functions are chosen, which can describe both valence and semicore states.

## II. THEORY

Let us explain this approach for the case of Sc, whose $3s$ state is a typical semicore state. The radial charge distribution $r^2|\Psi|^2$ of the $s$-wave functions is shown in Fig. 1.

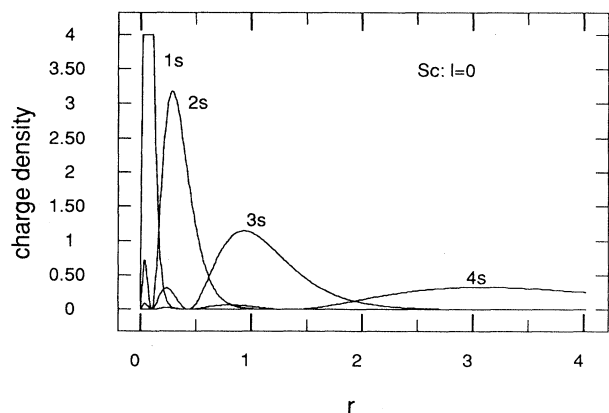A typical choice for the radius of the muffin-tin sphere



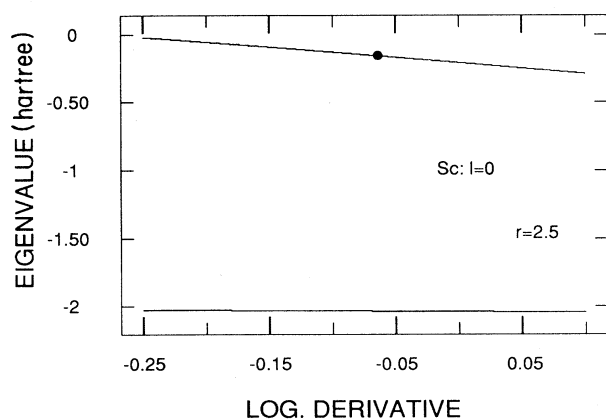FIG. 1. The radial charge distribution of the occupied $s$ states of Sc.

FIG. 2. The energy-vs-logarithmic derivative curve of the $l=0$ component of Sc for a muffin-tin radius of 2.5 a.u. The atomic $4s$ eigenvalue is denoted by a solid circle.
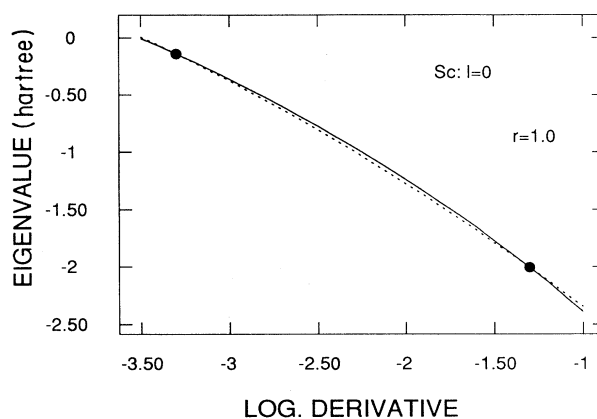


FIG. 3. The energy-vs-logarithmic derivative curve of the $l=0$ component of Sc for a muffin-tin radius of 1.0 a.u. The atomic reference eigenvalues are denoted by a solid circle. The solid line is the exact result and the dashed line is the result obtained with the linearized method.

would be $r_c=2.5$. In this case the $4s$ and $3s$ eigenvalues lie on different branches of the eigenvalue-versus-logarithmic derivative curve (Fig. 2) and therefore cannot be described by the usual linear method. If one chooses $r_c$ smaller than the first zero of the $4s$ wave function, both the $3s$ and $4s$ eigenvalues lie on the same branch of the eigenvalue-versus-logarithmic derivative curve, as shown in Fig. 3 for $r_c=1$.

We now choose as the basis in the muffin-tin sphere $u_{l,E_V}(r)$ and $u_{l,E_S}(r)$, which are the solutions of the radial Schrödinger equation at reference valence and semicore energies. Their expansion coefficients are determined by the continuity of the wave function and its derivative in the usual way. With this choice the eigenvalue-versus-logarithmic derivative curve given by this basis set coincides with the true eigenvalue-versus-logarithmic derivative curve at the two reference energies $E_V$ and $E_S$ (Fig. 3). The slopes, however, are not equal at the two reference energies [this would require adding $\dot{u}_{l,E_V}(r)$ and $\dot{u}_{l,E_S}(r)$ to the basis set]. As one sees, from Fig. 3, however, the slopes are not too wrong, since we have actually

replaced a derivative by a finite difference. Furthermore, physics comes to our aid. The dispersion of the $3s$ state is very small, i.e., its logarithmic derivative is nearly constant in different chemical environments. The two eigenvalue-versus-logarithmic derivative curves must therefore only match in a very tiny window around the semicore reference energy. The dispersion of the $4s$ state is of course much larger. However, it must be taken into account that the error of the eigenvalue must be weighted by the percentage of the charge of the $4s$ wave function contained in the muffin-tin sphere. Because this is typically a few percent, errors arising from the dispersion of the $4s$ state are also small even though the two eigenvalue-versus-logarithmic derivative curves deviate linearly.

## III. NUMERICAL EFFICIENCY

Choosing a smaller muffin-tin radius might seem unreasonable because it requires a larger number $N_P$ of

TABLE I. Numerical results.

| Element | Reference configuration | Configuration | Energy difference (hartree) | Error (hartree) |
|---|---|---|---|---|
| Sc | $4s^2 3p^6 3d^1$ | $4s^1 3p^6 3d^2$ | 0.054 | $1\times10^{-5}$ |
| Sc | $4s^2 3p^6 3d^1$ | $4s^{1.5} 3p^6 3d^1$ | 0.103 | $1\times10^{-7}$ |
| Sc | $4s^2 3p^6 3d^1$ | $4s^2 3p^6 3d^{1.5}$ | $-0.028$ | $2\times10^{-6}$ |
| Sc | $4s^2 3p^6 3d^1$ | $4s^2 3p^6 3d^{0.5}$ | 0.110 | $5\times10^{-6}$ |
| Mn | $4s^2 3p^6 3d^5$ | $4s^1 3p^6 3d^6$ | $-0.024$ | $8\times10^{-6}$ |
| Mn | $4s^2 3p^6 3d^5$ | $4s^1 3p^6 3d^5$ | 0.314 | $6\times10^{-7}$ |
| Mn | $4s^2 3p^6 3d^5$ | $4s^2 3p^6 3d^4$ | 0.505 | $1\times10^{-5}$ |
| Mn | $4s^2 3p^6 3d^5$ | $4s^2 3p^6 3d^{5.5}$ | $-0.053$ | $2\times10^{-6}$ |
| Y | $5s^2 4p^6 4d^1$ | $5s^1 4p^6 4d^2$ | 0.053 | $1\times10^{-6}$ |
| Y | $5s^2 4p^6 4d^1$ | $5s^1 4p^6 4d^1$ | 0.244 | $5\times10^{-7}$ |
| Y | $5s^2 4p^6 4d^1$ | $5s^2 4p^6 4d^{1.5}$ | $-0.026$ | $2\times10^{-7}$ |
| Y | $5s^2 4p^6 4d^1$ | $5s^2 4p^6 4d^{0.5}$ | 0.249 | $1\times10^{-5}$ |

plane waves. If a conventional approach is used, where the computational effort grows as $N_P^3$, the computer time would certainly increase too much. If, however, the operator approach[5] is used, where the numerical effort grows only like $N_P\log_2(N_P)$, the program might even get faster, since $l_{max}$ can be reduced.

## IV. RESULTS

These theoretical arguments are confirmed by the following numerical results. We compared the energies of several ionized and excited transition-element atoms with and without the linear approximation. The results without any approximations were obtained by a standard nonrelativistic atomic density functional program. The results of the linearized method were obtained by a similar program that used $u_{l,E_V}(r)$ and $u_{l,E_S}(r)$ functions in the muffin-tin region as basis functions and Hermite finite elements[6] outside the sphere. This approach has the advantage that it eliminates other sources of errors and that one can obtain very precise results. The $u_{l,E_V}$ and $u_{l,E_S}$ for the $l=0$ component were calculated at the reference energies of neutral atoms in the ground state. For all other $l$ components the usual $u_l$ and $\dot{u}_l$ functions were used. The radius of the muffin-tin sphere was chosen such that 99.9% of the core charge was contained in the sphere. With this choice of reference energies the linearized method gives the exact result for the ground state of the neutral atom. For all the other configurations the error was smaller than $10^{-5}$ hartree (Table I), which is comparable to the error arising from the frozen-core approximation.

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