

# Relativistic analyse of extended norm-conserving pseudo-potentials

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Extended norm-conserving pseudopotentials developed by E. L. Shirley et al. [1] in non relativistic case, is obtained in present work in the relativistic case. We discuss the importance of the added relativistic terms and we carry out a test of this new extension on some transition-metal atoms. This correction enables us to adapt norm-conserving properties for relativistic pseudopotential used in the LDA (local-density approximation)[2] context.

## I. INTRODUCTION

A pseudopotentials (PP) were originally introduced to simplify electronic structure calculations by eliminating the need to include atomic core states and the strong potentials responsible for binding[3]. The widely used norm-conserving pseudopotentials (NCPP) have several desirable properties[4]. They satisfy a transferability criterion[4], which ensures that the NCPP reproduce correctly the full atom potential scattering power at energies away from the bound-valence-state energy (to first order in the energy difference). E. L. Shirley et. al.[1] showed that it is possible to extend this energy range in the hope of reducing errors in the single-body properties of a NCPP..

The first relativistic LDA version of the PP approach, where the corresponding coupled relativistic equations for the valence electrons were transformed into the non-relativistic Schrödinger equation, was suggested by L. Kleinman[5] and realised numerically by G. B. Bachelet et. al.[6]. This approach is not well grounded for the core region where the d component of the PP is quite substantial, reaching e.g. hundred of Rydbergs for 3d elements[7]. Moreover, the procedure suggested by V. Yu. Milman et. al.[8] shows that in the core region the PP magnitude is not negligible when it is compared to fine structure contribution ( $\alpha^2$ ) for some transition-metals. It was noticed that the systems with 1s, 2p, 3d or 4f valence states are represented only by hard PP[9,10]. The PP magnitude in the core region of these states leads us to revise the suggestion developed by L. Kleinman, especially for the hard PP transferability-criterion.

In this work, we establish a relativistic version of the extended norm-conserving pseudo-potential developed early by E. L. Shirley et. al.[1]. The relativistic corrections are found to be significant for the three transition metal atoms: iron, zirconium and platinum.

## II. THEORETICAL BACKGROUND

For a central potential  $V(r)$ , the Dirac equation reduces to two coupled radial equations for  $\phi$  and  $F$ , the radial parts of the major and minor Dirac wave functions components in the standard representations and in atomic units ( $c = \alpha^{-1} = 137.037$ );  $k$  is the spin-orbit quantum number, equal to  $l$  (angular momentum) for  $j = l - \frac{1}{2}$  and  $-(l+1)$

for  $j = l + \frac{1}{2}$  such as:

$$\frac{dF(r)}{dr} = \frac{k}{r} F(r) - \alpha(E - V(r))\phi(r) \quad (1)$$

$$\frac{d\phi(r)}{dr} = \alpha \left( \frac{2}{\alpha^2} + E - V(r) \right) F(r) - \frac{k}{r} \phi(r)$$

After substitution of the  $F$  expression which is deduced from the second equation, in the first equation of the set (1), we obtain the second order differential equation which generates major part  $\phi$ , expressed in presence of a spherical perturbation as:

$$-\frac{d^2}{dr^2} \phi(r) - \frac{2}{\alpha^2} \frac{dV(r)}{dr} \left( \frac{d\phi(r)}{dr} + \frac{k}{r} \phi(r) \right) + \left( \frac{l(l+1)}{2} + 2M(V(r)-E) \right) \phi(r) = 0 \quad (2)$$

where  $\phi(r)$  is  $r$  times radial wave function and

$$M = 1 - \frac{\alpha^2}{2} (V(r) - E)$$

Equation (2) is more general. The scalar relativistic case ensues directly if one replaces  $k$  by  $-1$  (the spin-orbit term is averaged).

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We shall describe the  $V(r)$  scattering properties through the  $\phi$  radial-logarithmic derivative, i.e:  $\phi'/\phi$ , which we shall call  $x$ . Integrating the non-singular solution of (2) from zero to a given atomic core radius  $R$ , one obtains some value of  $x$  at  $R$ . Then the equation (2) can be written as a first-order non-linear differential equation in  $x$  which is analogous to one obtained in non-relativistic case[1]:

$$x' + x^2 + \frac{\alpha^2}{2M} \frac{dV}{dr} \left(x + \frac{k}{r}\right) = W \quad (3)$$

with,

$$\begin{aligned} \frac{\partial x(R)}{\partial E} = & -\frac{2}{\phi^2(R)} \int_0^R dr \phi^2(r) + \frac{2\alpha^2}{\phi^2(R)} \int_0^R dr \phi^2(r) (V-E) \\ & - \frac{1}{\phi^2(R)} \int_0^R dr \phi^2(r) \frac{dV}{dr} \left( \frac{\alpha^2}{2M} \frac{\partial x(r)}{\partial E} - \left( \frac{\alpha^2}{2M} \right)^2 \left( x(r) + \frac{k}{r} \right) \right) \end{aligned} \quad (6)$$

This equation is valid for nodeless wave functions inside  $R$ . One can continue differentiation of (3) to get the following relation for all higher orders in  $E$ :

$$\begin{aligned} x^{(n)}(R) = & -\frac{1}{\phi^2(R)} \sum_{p=1}^{n-1} \binom{n}{p} \int_0^R dr \phi^2(r) x^{(p)}(r) x^{(n-p)}(r) \\ & - \frac{1}{\phi^2(R)} \int_0^R dr \phi^2(r) \left\{ -W^{(n)} + \left( \frac{\alpha^2}{2M} \right) \frac{dV}{dr} \left[ x^{(n)}(r) + A_n n! \left( x(r) + \frac{k}{r} \right) \right] \right\} \end{aligned} \quad (7)$$

$$- \frac{1}{\phi^2(R)} \sum_{p=1}^{n-1} \binom{n}{p} \int_0^R dr \phi^2(r) A_p p! \left( \frac{\alpha^2}{2M} \right) \frac{dV}{dr} x^{(n-p)}(r)$$

where  $x^{(n)}(R)$  and  $W^{(n)}(R)$  represent respectively the  $n$  order of  $x$  and  $W$  derivatives at  $R$  with respect to  $E$ . The  $A_n$  coefficient was expressed in the form:

$$A_n = (-1)^n \left( \frac{\alpha^2}{2M} \right)^n$$

For example, the second and third energy derivatives of  $x$ , which are the most used in practice, are written respectively as:

$$\frac{\partial^2 x(R)}{\partial E^2} = -\frac{2}{\phi^2(R)} \int_0^R dr \phi^2(r) \left( \frac{\partial x(r)}{\partial E} \right)^2 \quad (8)$$

$$- \frac{1}{\phi^2(R)} \int_0^R dr \phi^2(r) \left\{ 2\alpha^2 + \left( \frac{\alpha^2}{2M} \right) \frac{dV}{dr} \left[ \frac{\partial^2 x(r)}{\partial E^2} - 2 \left( \frac{\alpha^2}{2M} \right) \frac{\partial x(r)}{\partial E} + 2 \left( \frac{\alpha^2}{2M} \right)^2 \left( x(r) + \frac{k}{r} \right) \right] \right\}$$

and

$$\begin{aligned} \frac{\partial^3 x(R)}{\partial E^3} = & -\frac{6}{\phi^2(R)} \int_0^R dr \phi^2(r) \frac{\partial^2 x(r)}{\partial E^2} \frac{\partial x(r)}{\partial E} \\ & - \frac{1}{\phi^2(R)} \int_0^R dr \phi^2(r) \left( \frac{\alpha^2}{2M} \right) \frac{dV}{dr} \left[ \frac{\partial^3 x(r)}{\partial E^3} - 3 \left( \frac{\alpha^2}{2M} \right) \frac{\partial^2 x(r)}{\partial E^2} + 6 \left( \frac{\alpha^2}{2M} \right)^2 \frac{\partial x(r)}{\partial E} \right] \\ & + \frac{6}{\phi^2(R)} \int_0^R dr \phi^2(r) \left( \frac{\alpha^2}{2M} \right)^4 \frac{dV}{dr} \left( x(r) + \frac{k}{r} \right) \end{aligned} \quad (9)$$

Equations (6), (7), (8) and (9) constitute a new relativistic extension of the analogous

$$W = \frac{l(l+1)}{r^2} + 2M(V(r)-E) \quad (4)$$

Using the relation valid for any function  $f(r)$ ,

$$f'(r) + 2 \frac{\phi'(r)}{\phi(r)} f(r) = \frac{1}{\phi^2(r)} \frac{d}{dr} (\phi^2(r) f(r)) \quad (5)$$

and differentiating (3) once with respect to  $E$  one obtains, after multiplying by  $\phi^2(r)$  and integrating, the following equation:

transferability criterion obtained in non-relativistic pseudopotential developed previously by E. L.

Shirley et. al.[1]. We remark that the method introduced to build these equations is performed at arbitrary energies sign, thus they remain valid for both bound and unbound states.

It is well-known that in a norm-conserving PP, the total charge inside R, is the same for the pseudo wave function as well as for the full-atomic wave function, what is explained according to transferability criterion by the scattering properties conservation. These properties are defined as an energy derivative of the wave function radial-logarithmic derivative. In relativistic case, this direct consequence does not persist owing to the added terms in second member of (6). Thus, the conservation of the total charge is fulfilled in passing from a configuration to another, only if we conserve all this second member. Consequently, the equation (6) represent a transferability criterion of

$$RT_n = -\frac{1}{\phi^2(R)} \int_0^R dr \phi^2(r) \left\{ -W^{(n)} + \left( \frac{\alpha^2}{2M} \right) \frac{dV}{dr} \left[ x^{(n)}(r) + A_{nn}!(x(r) + \frac{k}{r}) \right] \right\} \\ - \frac{1}{\phi^2(R)} \sum_{p=1}^{n-1} \binom{n}{p} \int_0^R dr \phi^2(r) A_{pp} \left( \frac{\alpha^2}{2M} \right) \frac{dV}{dr} x^{(n-p)}(r) \quad (10-b)$$

$RT_n$  are explicitly potential depend. We suggest that the use of this relativistic contribution is more important for systems which have 1s, 2p, 3d, 4f or 5g valence wave functions requiring deep pseudopotentials because these wave functions are nodeless in the radial direction and the pseudopotential obtained cannot soften the electron-nuclear interaction by eliminating oscillations in the wave functions and thereby reducing the corresponding kinetic energy[9]. Otherwise, the  $RT_n$  terms contain the same n order derivation of  $x(r)$  inside atomic sphere, thus in present case one cannot readily see the iterative hierarchical schem needed to achieve analytic expression of all derivatives as could be obtained for  $NRT_n$  terms alone.

The implementation of this extended norm-conserving in relativistic PP approach[8] could be carried out by forcing the high order  $x(r)$  energy derivatives to be equal to those corresponding to the true wave function, in a way similar to that realised in non relativistic case using the generalized Vanderbilt's form of the envelope function[12] or the improved form used by E. L. Shirley et al.[1].

Equations (6), (7), (8) and (9) could be generalized to be applicable also to wave functions with nodes when taking second and higher order derivatives. Through a node, the integrand must be integrated carefully by using a procedure suggested by M. Y. Chou[13], which is based on a minimisation of the difference between true and pseudo-wave functions radial-logarithmic derivatives. This suggests that this formalism

relativistic PP. So we would call it the first order relativistic transferability criterion. Equations (8) and (9) are called similarly second and third order relativistic transferability criterion respectively.

Equation (7) states that any  $n \geq 2$  order derivative of  $x$  can be separate in two parts: (i) The non-relativistic terms ( $NRT_n$ ) are expressed as a sum of integrals of products containing  $\phi^2(r)$  times pairs of lower  $x(r)$  derivatives, like that obtained previously in non-relativistic case[1]:

$$NRT_n = -\frac{1}{\phi^2(R)} \sum_{p=1}^{n-1} \binom{n}{p} \int_0^R dr \phi^2(r) x^{(p)}(r) x^{(n-p)}(r) \quad (10-a)$$

(ii) The relativistic terms ( $RT_n$ ), that we established in this work can be expressed as:

remain valid for NCPP with pseudowave functions conserving nodes in the radial direction[14].

### III.APPLICATION

To analyse the relativistic contribution importance to the transferability criterion, we carry out an application on some transition metals (Iron, Zirconium and Platinum). In background state, we used the waves and eigenvalues obtained by the self-consistently resolved Dirac equations. We compare relativistic onto non-relativistic terms appearing in second members of the criterions (6), (8) and (9), by using the ratios

$$\Delta_1 = \frac{RT_1}{NRT_1}, \Delta_2 = \frac{RT_2}{NRT_2} \text{ and } \Delta_3 = \frac{RT_3}{NRT_3}$$

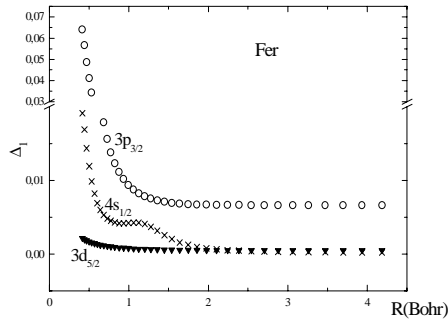
measuring the importance of the relativistic contribution corresponding respectively to first, second and third relativistic corrections.

#### 1. 1. First order effects: $\Delta_1$

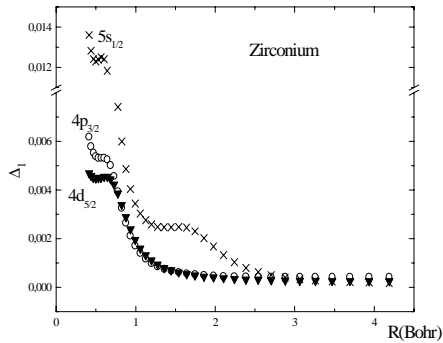
Figures 1, 2 and 3 show the calculated first order behaviour vs R. The  $\Delta_1(R)$  oscillations in the nucleus proximity ( $R = 0$ ), due essentially to the oscillatory character of atomic wave functions in this region, extend over a specific radii  $R_C$  dependent on the considered atom and representing an effective nuclear scattering range. Notice that a "cut-off radius"  $R_C$  is generally used in the pseudopotential approach. It ranges between 0.8 and 2.4 u.a.[ 6, 16 -17 ], where the relativistic contribution magnitude remains near to the fine structure constant ( $\alpha^2$ ) value. Then, by going away

more and more from atomic core we can distinguish between two zones : The first one corresponding to radii  $R > R_C$  is characterized by predominance of the kinetic relativistic effect while in the second zone ( $R < R_C$ ), the other relativistic terms ( Darwin and spin-orbit) are dominant.

Consequently, the non-null asymptotic tendency (for  $R \gg R_C$ ) of  $\Delta_1(3p_{3/2})$  compared with that of  $\Delta_1(4s_{1/2})$  and  $\Delta_1(3d_{5/2})$  which are almost null in the Fe case (fig.1) can be explained by the important kinetic relativistic character of the  $3p_{3/2}$  state which is deeper energetically than  $4s_{1/2}$  and  $3d_{5/2}$  states. Generally, the deepest states present a more pronounced kinetic relativistic effect. What is expressed also by a corresponding  $\Delta_1(R)$  non null asymptotic values for  $4p_{3/2}(\text{Zr})$  and  $4f_{7/2}(\text{Pt})$  cases (fig 2 and 3 respectively) .



**Figure 1**  $\Delta_1$  versus  $R$  for the  $4s_{1/2}$ ,  $3p_{3/2}$  and  $3d_{5/2}$  states calculated for iron.

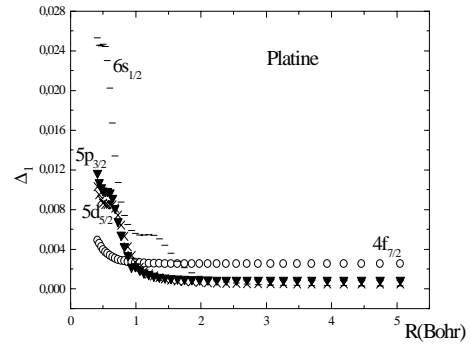


**Figure 2**  $\Delta_1$  versus  $R$  for the  $5s_{1/2}$ ,  $4p_{3/2}$  and  $4d_{5/2}$  states calculated for zirconium.

any electronic structure calculation using a PPNC relativistic approach would be necessary.

## 2. Second order effects: $\Delta_2$

The results corresponding to second order relativistic effects  $\Delta_2$  are presented on figures 4, 5 and 6 respectively for the same considered atoms. We see that the  $\Delta_2$  radial evolution is very sensitive to the valence state angular momentum value. Indeed, the ns states (for the three atoms) present the weakest relativistic contribution which is an



**Figure 3**  $\Delta_1$  versus  $R$  for the  $6s_{1/2}$ ,  $5p_{3/2}$  and  $5d_{5/2}$  states calculated for platinum.

Furthermore, in the first zone we notice that a valence state evolution is nearly atomic radii independent, while in the second zone this evolution is highly  $R$  dependent for different  $l$  values. This behaviour could be explained by the important angular dependence of the power electronic scattering in atomic nucleus proximity. Otherwise, from the comparison between figures 1, 2 and 3 we notice that in passing from iron ( $Z = 26$ ) to zirconium ( $Z = 40$ ) and to platinum ( $Z = 78$ ) a net change in  $\Delta_1(R)$  evolution is observed. Indeed, even for the states with the same angular momentum, there is a net variation of the atomic radii value accompanying the successive growth of the radial nodes number of the wavefunctions in passing from the  $(n)$  to the  $(n+1)$  level. The increase of the radial nodes number has for consequence to make more complex the  $\frac{\partial x}{\partial E}(R)$  behaviour inside the atomic sphere.

We notice also that the  $\Delta_1$  value remains above  $\alpha^2$  for the three studied atoms despite the notable difference between their atomic numbers  $Z$ . Consequently, the introduction of the explicit relativistic terms contribution in the pseudopotential transferability rules as well as in

atomic sphere area independent, while the np, nd and nf states reveal a more important relativistic contribution.

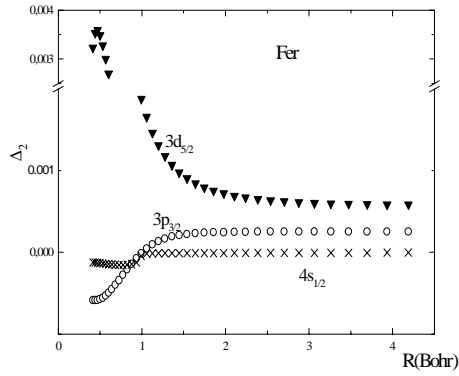
The separation of the second order effect behaviour in two zones remains also possible with a light difference between "separation radius". However and for three considered atoms,  $\Delta_2(R)$  behaves differently when it is compared with the first order effect  $\Delta_1(R)$ .

Thus, the hierarchical dependence on  $\frac{\partial^2 x}{\partial E^2}(r)$  and  $x(r)$  of the  $\frac{\partial^2 x}{\partial E^2}(R)$  function can be the

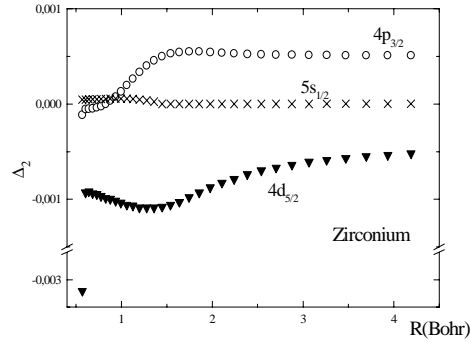
origin of  $\Delta_2(R)$  oscillatory character in the neighbourhood of atomic nucleus resulting at once from the behaviours shown by the atomic wave functions and  $\frac{\partial x}{\partial E}(r)$  extremes in  $r < R_c$  range.

These oscillations are more complicated by change in  $\Delta_2(R)$  sign and by an important modification of the relativistic effect value for the same state in passing from the first ( $\Delta_1$ ) to second order ( $\Delta_2$ ).

This hierarchical dependence has also for consequence a supplementary effect (to that corresponding to  $\Delta_1$ ) on the asymptotic limits evolution of  $\Delta_2(R)$  beyond  $R_c$  radii. These limits become hear clearly more discerned for different  $l$  values (fig. 4, 5 and 6).



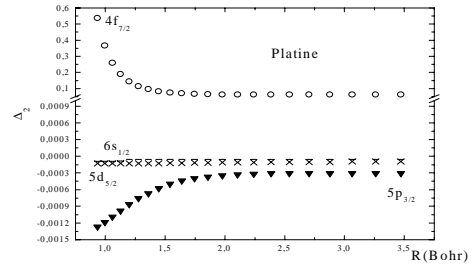
**Figure 4**  $\Delta_2$  versus  $R$  for the  $4s_{1/2}$ ,  $3p_{3/2}$  and  $3d_{5/2}$  states calculated for iron.



**Figure 5**  $\Delta_2$  versus  $R$  for the  $5s_{1/2}$ ,  $4p_{3/2}$  and  $4d_{5/2}$  states calculated for zirconium.

### 3. Third order effects: $\Delta_3$

The figures 7, 8 and 9 show that, as in the preceding case, the  $\Delta_3(R)$  evolution is very sensitive to the angular momentum state. The ns states present a minimal relativistic contribution compared to that observed in the non null angular momentum states.



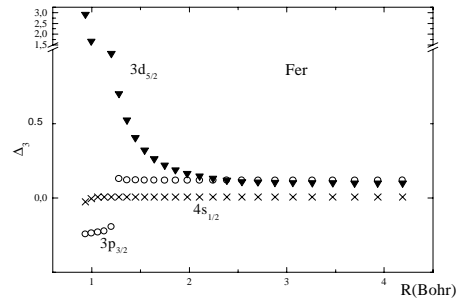
**Figure 6**  $\Delta_2$  versus  $R$  for the  $6s_{1/2}$ ,  $5p_{3/2}$  and  $5d_{5/2}$  states calculated for platinum.

$$\Delta_3(R) \text{ expression results from } \frac{\partial^3 x}{\partial E^3}(R)$$

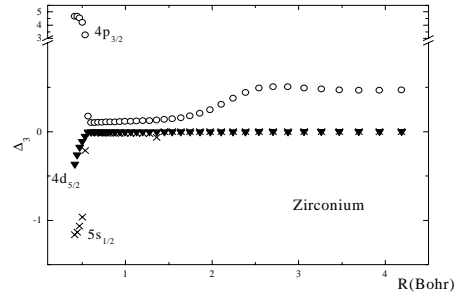
which depends hierarchically on  $\frac{\partial^2 x}{\partial E^2}(r)$ ,  $\frac{\partial x}{\partial E}(r)$  and

$x(r)$  functions increasing the complexity shown by the  $\Delta_3(R)$  behaviour (inherited from  $\Delta_2(R)$  and  $\Delta_1(R)$ ) essentially in the second zone ( $R < R_c$ ) and affect the  $\Delta_3(R)$  asymptotic limits evolution for  $R > R_c$  (first zone) in spite of the kinetic relativistic term absence in  $RT_3(R)$ .

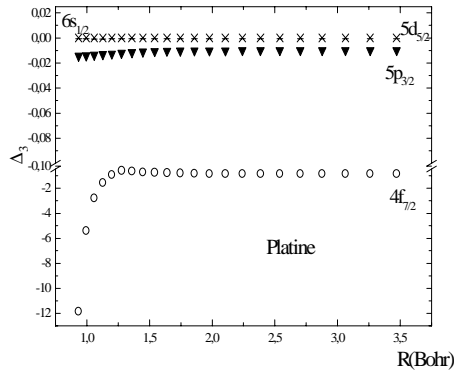
Through this test, we concluded that the relativistic contribution cannot be neglect completely in the pseudopotential transferability.



**Figure 7**  $\Delta_3$  versus  $R$  for the  $4s_{1/2}$ ,  $3p_{3/2}$  and  $3d_{5/2}$  states calculated for iron.



**Figure 8**  $\Delta_3$  versus  $R$  for the  $5s_{1/2}$ ,  $4p_{3/2}$  and  $4d_{5/2}$  states calculated for zirconium.



**Figure 9**  $\Delta_3$  versus  $R$  for the  $6s_{1/2}$ ,  $5p_{3/2}$  and  $5d_{5/2}$  states calculated for platinum.

#### 4. CONCLUSION

In this work, we establish the relativistic correction of the extended norm-conserving-pseudopotential. We discuss the implementation of this extension in the relativistic PP scheme. We test the importance of this relativistic contribution through an application carried out on iron, zirconium and platinum which shows that this correction improves the precision as well as the extension of the relativistic PP transferability to one, two and three order.

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