Norm-conserving Pseudopotential

12/4/98

[N. Troullier & J. L. Martins, Phys. Rev. B43, 1993-2006 ('91)]

- Prerequisites

All-electron, self-consistent calculation has produced

$R_{nl}(r)$: Radial eigenstates

E_{nl} : Eigenstates

including all occupied bands and some empty orbitals with energies closed to the Fermi energy.

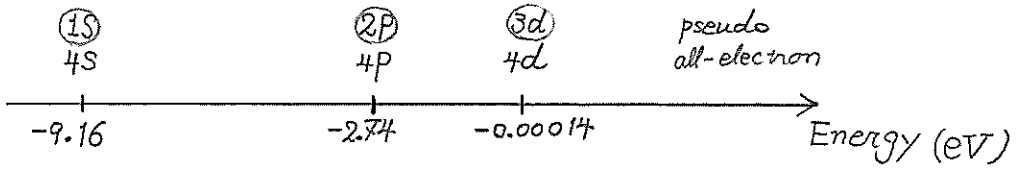
For example, consider Ga (Z=31). The all-electron calculation involves

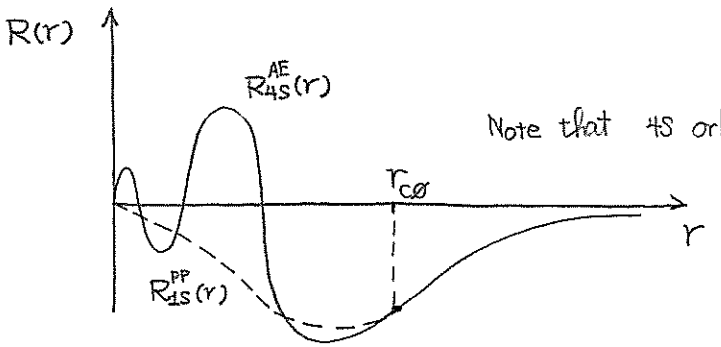
$$\underbrace{(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^{10}}_{\text{core (28)}} \quad \underbrace{(4s)^2(4p)^1}_{\text{valence (3)}} \quad \underbrace{(4d)^0}_{\text{extra (0)}}$$

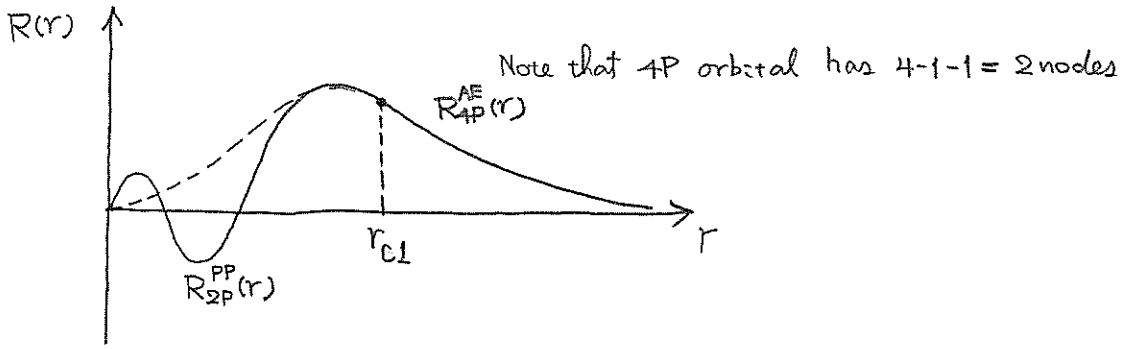
(We assume that all $m=\pm1,0$ states in the 4p orbital are equally occupied to produce a spherically symmetric self-consistent potential.)

Pseudopotential

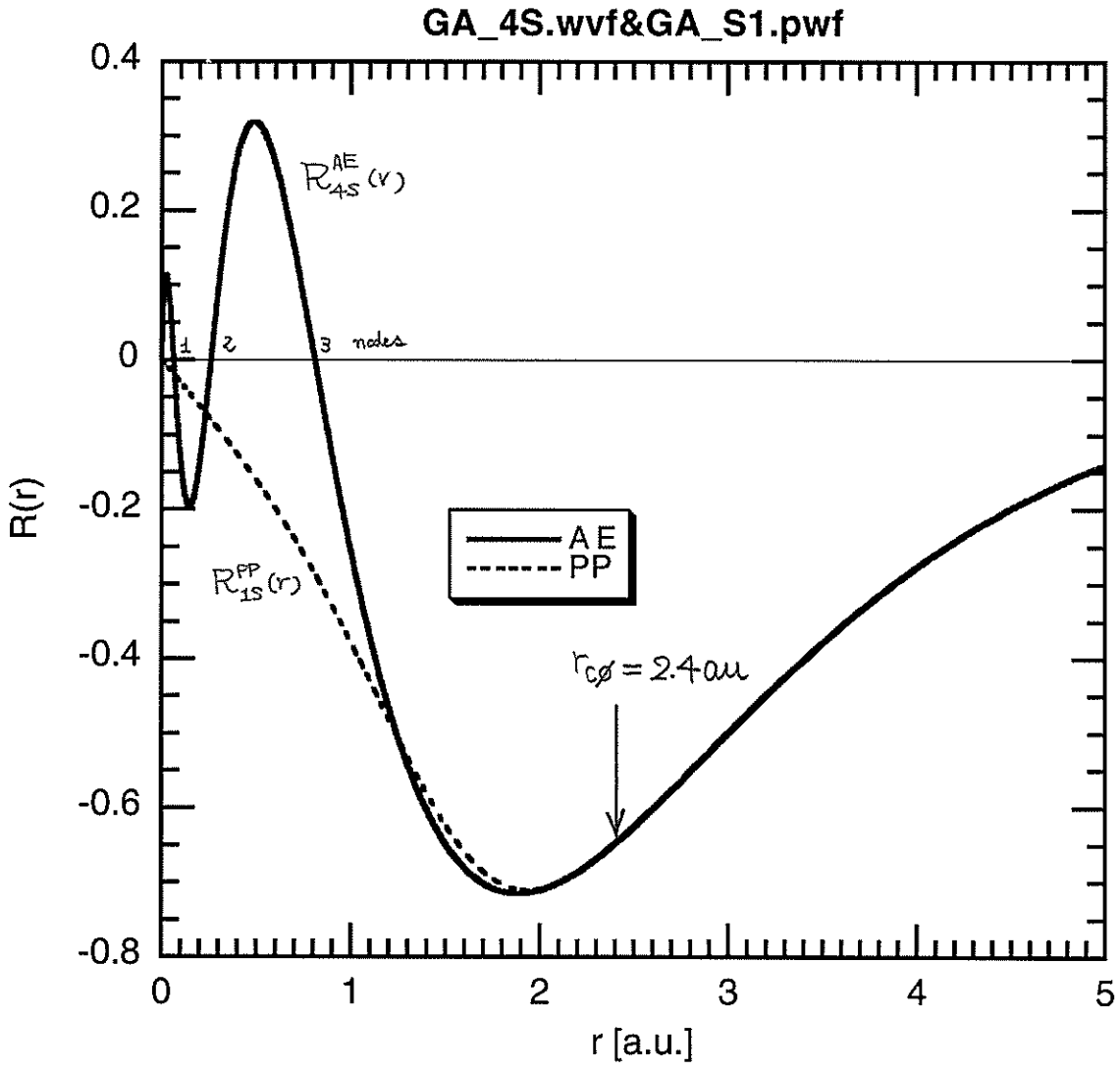
Construct pseudopotentials, $V^{PP}_{ion,l}(r)$ $(l=0,1,2)$, the ground states $(n'=n-l-1=0)$ of which, $R^{PP}_{n=4+1,l}(r)$ $(l=0,1,2)$, coincide with the all-electron valence states, $R^{AE}_{4l}(r)$ $(l=0,1,2)$, beyond angular-momentum-dependent cutoff radii, r_{cl} $(l=0,1,2)$.

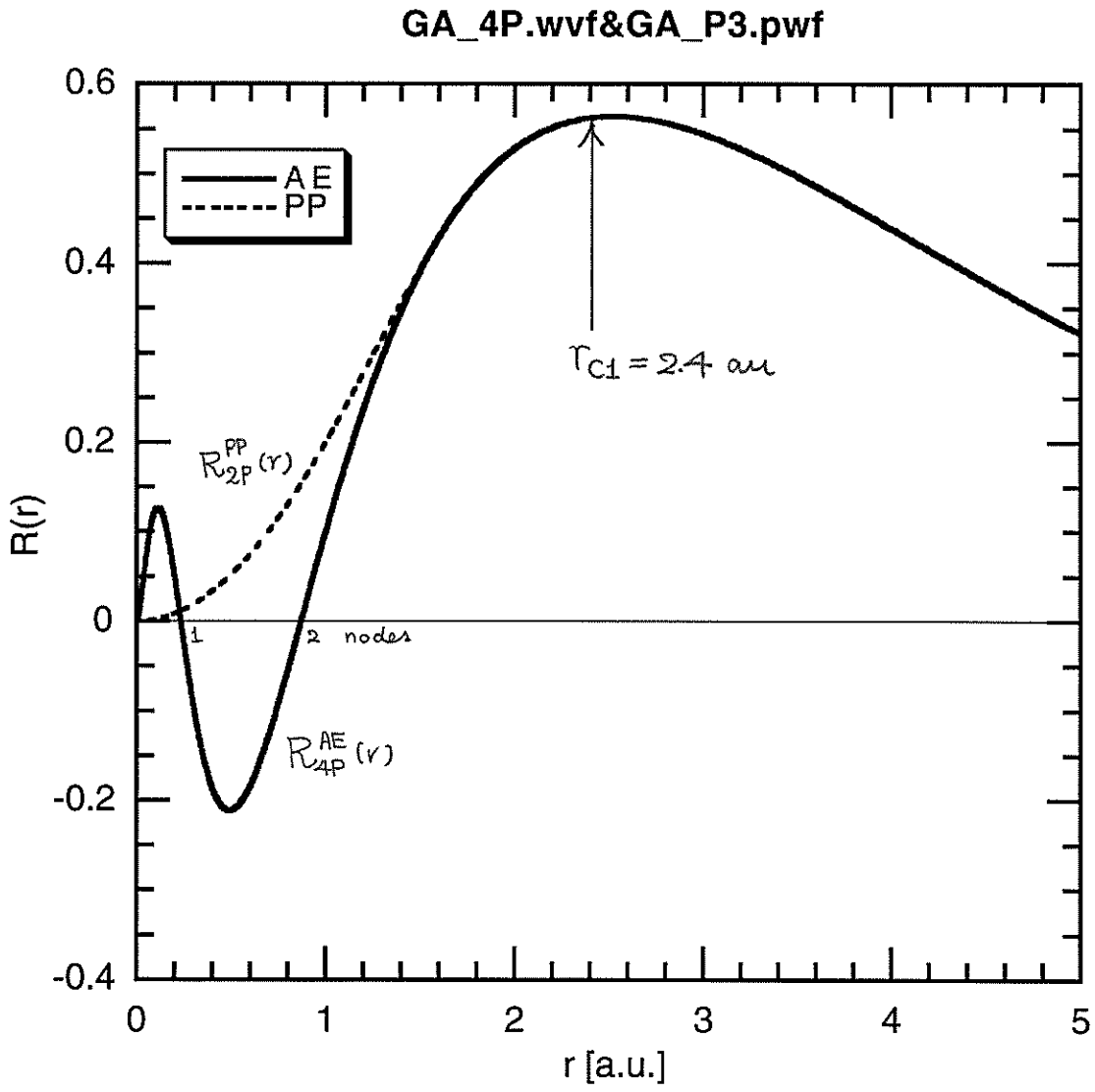


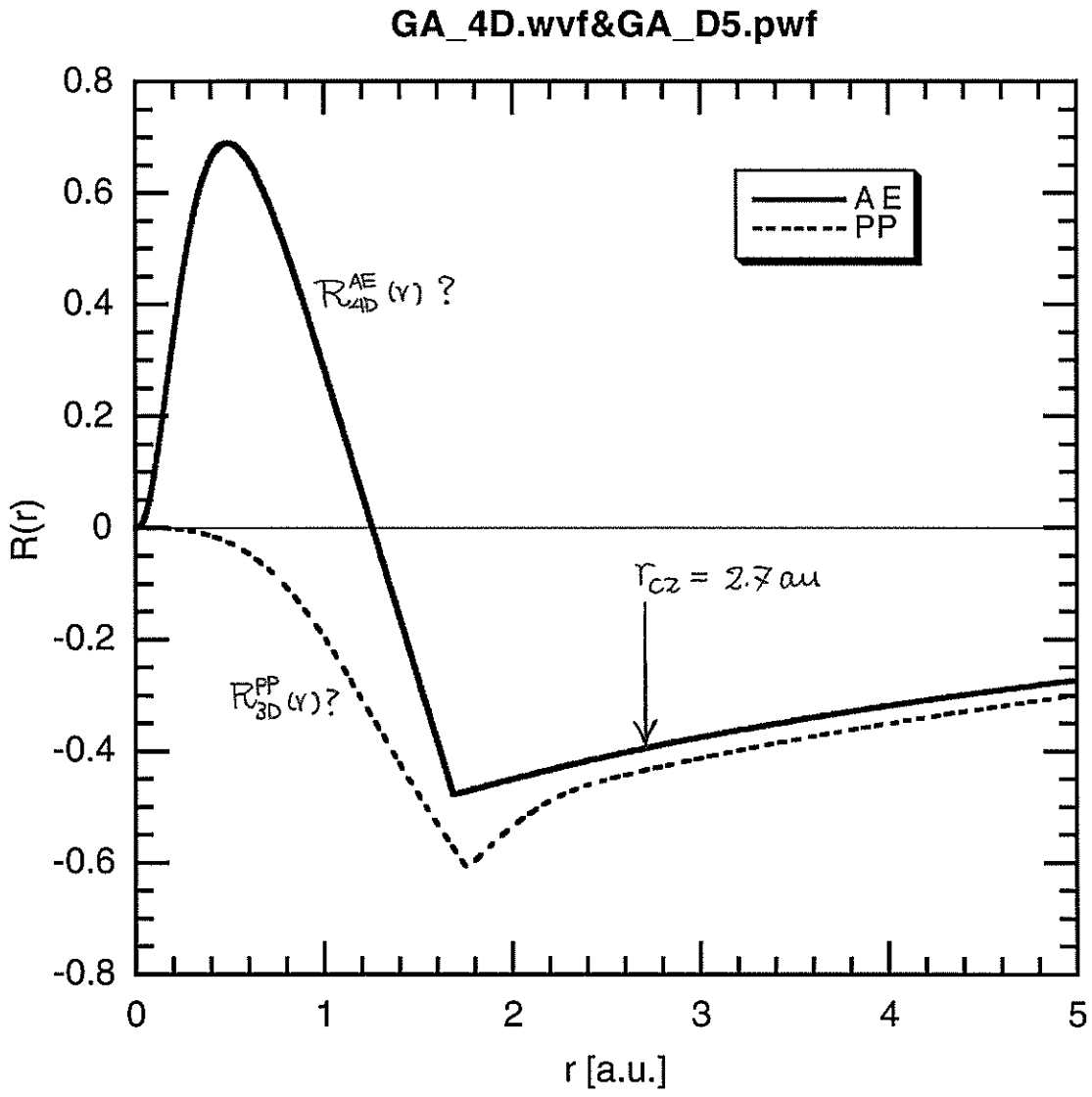




In chemically significant energy range, ± Hartree (13.6eV), electron wave functions in solids near a Ga atom can be constructed as a linear combination of $R^{AE}_{4l}(r)$ $(l=0,1,2)$. This is well reproduced by $R^{PP}_{n=4+1,l}(r)$ $(l=0,1,2)$ in the presence of $V^{PP}_{ion,l}(r)$ $(l=0,1,2)$, for which both the energies (hence the perturbation behavior) and wave functions for chemically active ranges are correct.


GA_4S.wvf&GA_S1.pwf
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
R(r)
0
1
2
3
4
5
r [a.u.]
$R^{AE}_{4S}(r)$
1
2
3 nodes
AE
PP
$R^{PP}_{1S}(r)$
$r_{c\phi} = 2.4 au$


GA_4P.wvf&GA_P3.pwf
AE
PP
$r_{C1} = 2.4$ au
$R^{PP}_{2P}(r)$
$R^{AE}_{4P}(r)$
1
2 nodes
R(r)
r [a.u.]
0.6
0.4
0.2
0
-0.2
-0.4
0
1
2
3
4
5


GA_4D.wvf&GA_D5.pwf
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
R(r)
0
1
2
3
4
5
r [a.u.]
AE
PP
$R^{AE}_{4D}(r)$?
$R^{PP}_{3D}(r)$?
r_{cz} = 2.7 au

— Requirement

1. Pseudowavefunctions, $R_l^{PP}(r)$ ($l=0,1,2$), contain no nodes.
(We omit the principal quantum number, $n=0+l+1$.)

2. The pseudo wavefunction, $R_l^{PP}(r)$, is equal to the all-electron wavefunction, $R_l^{AE}(r)$, beyond a chosen cutoff radius, r_{cl}.

$$R_l^{PP}(r) = R_l^{AE}(r) \quad \text{for} \quad r > r_{cl} \tag{1}$$

3. The charge enclosed within r_{cl} for the AE- and pseudo-wave-functions must be equal

$$\int_0^{r_{cl}} 4\pi r^2 dr \left|R_l^{PP}(r)\right|^2 = \int_0^{r_{cl}} 4\pi r^2 dr \left|R_l^{AE}(r)\right|^2 \tag{2}$$

4. The valence-electron AE- and pseudo-eigen values must be equal

$$E_l^{PP} = E_l^{AE} \tag{3}$$

Condition 2, in particular, requires that the logarithmic derivative of the two eigenfunctions must match at r_{cl}

$$\frac{1}{R_l^{PP}(r,E_l)} \frac{dR_l^{PP}(r,E_l)}{dr}\bigg|_{r=r_c} = \frac{1}{R_l^{AE}(r,E_l)} \frac{dR_l^{AE}(r,E_l)}{dr}\bigg|_{r=r_c} \tag{4}$$

$E_l \equiv E_l^{PP} = E_l^{AE}$

Condition 3 guarantees that the energy dependence of the logarithmic derivative is also correct up to the linear term near $E = E_{nl}$.

☺
$$-\frac{\hbar^2}{2m}\frac{\partial}{\partial E}\frac{\partial R_l(r,E)/\partial r}{R_l(r,E)}\bigg|_{\substack{r=r_c \\ E=E_l}} = \frac{1}{4\pi r_{cl}^2 R_l^2(r_{cl},E_c)} \int_0^{r_c} 4\pi r^2 dr\, R_l^2(r,E_l) \tag{5}$$

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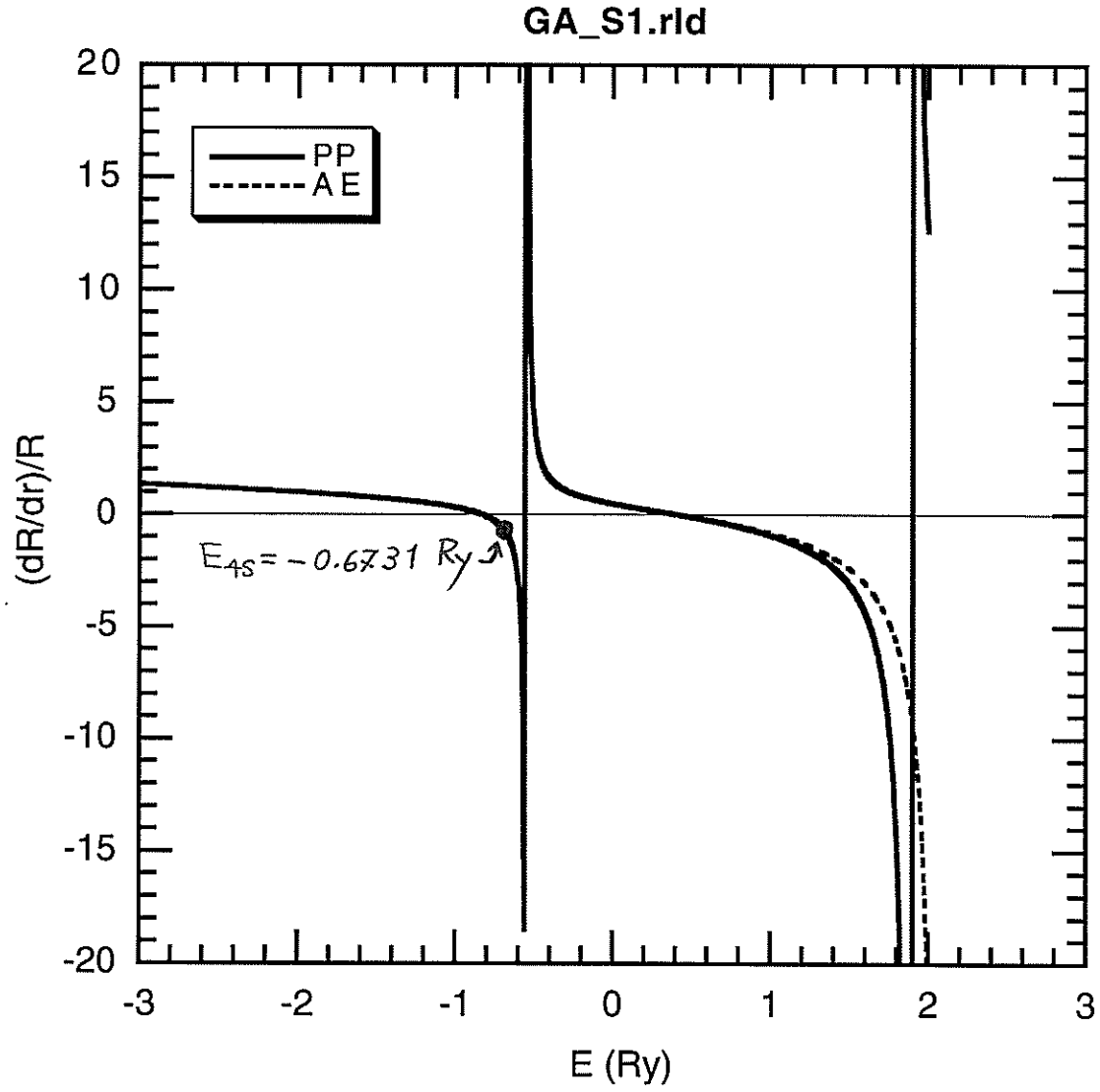
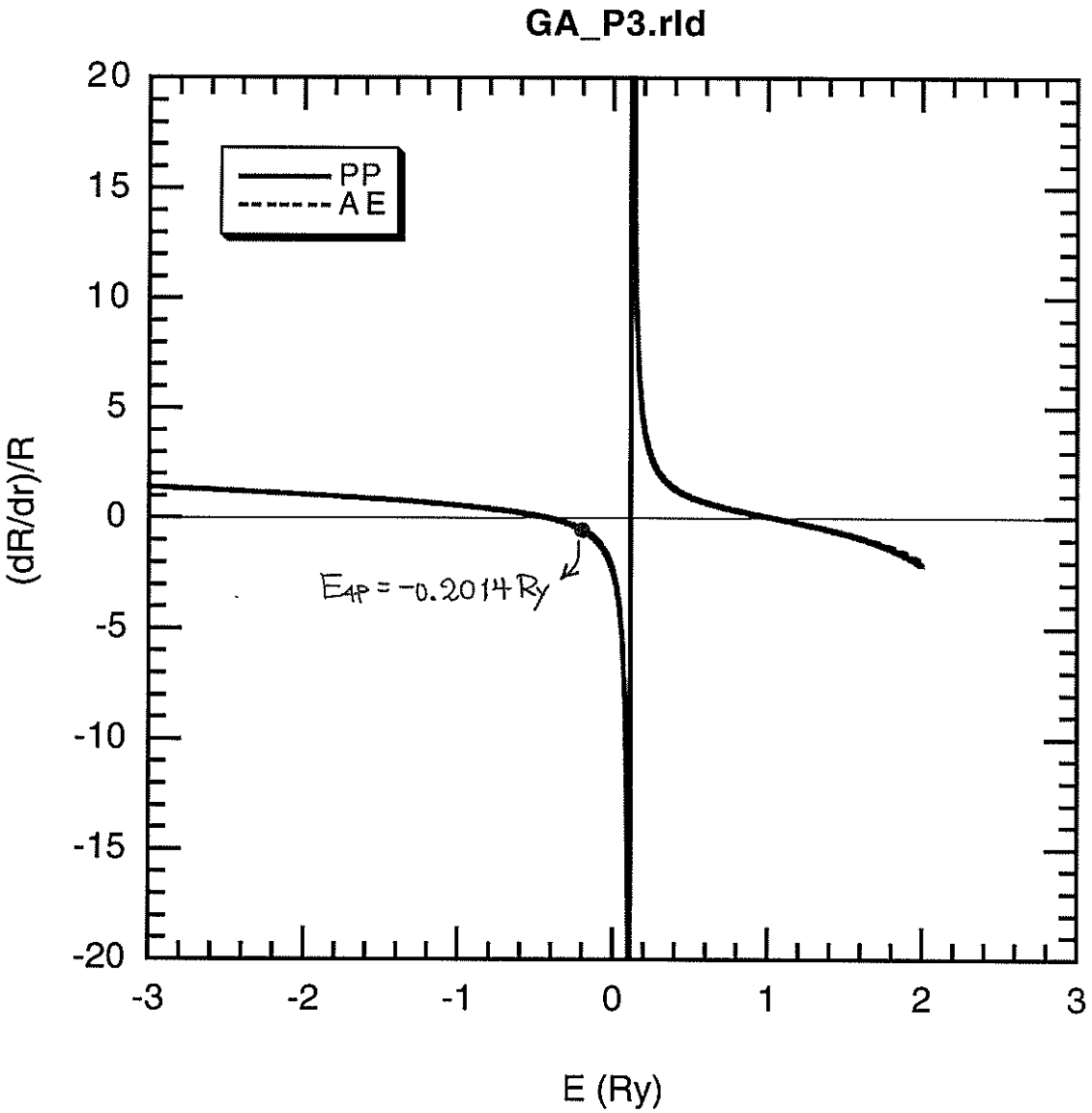
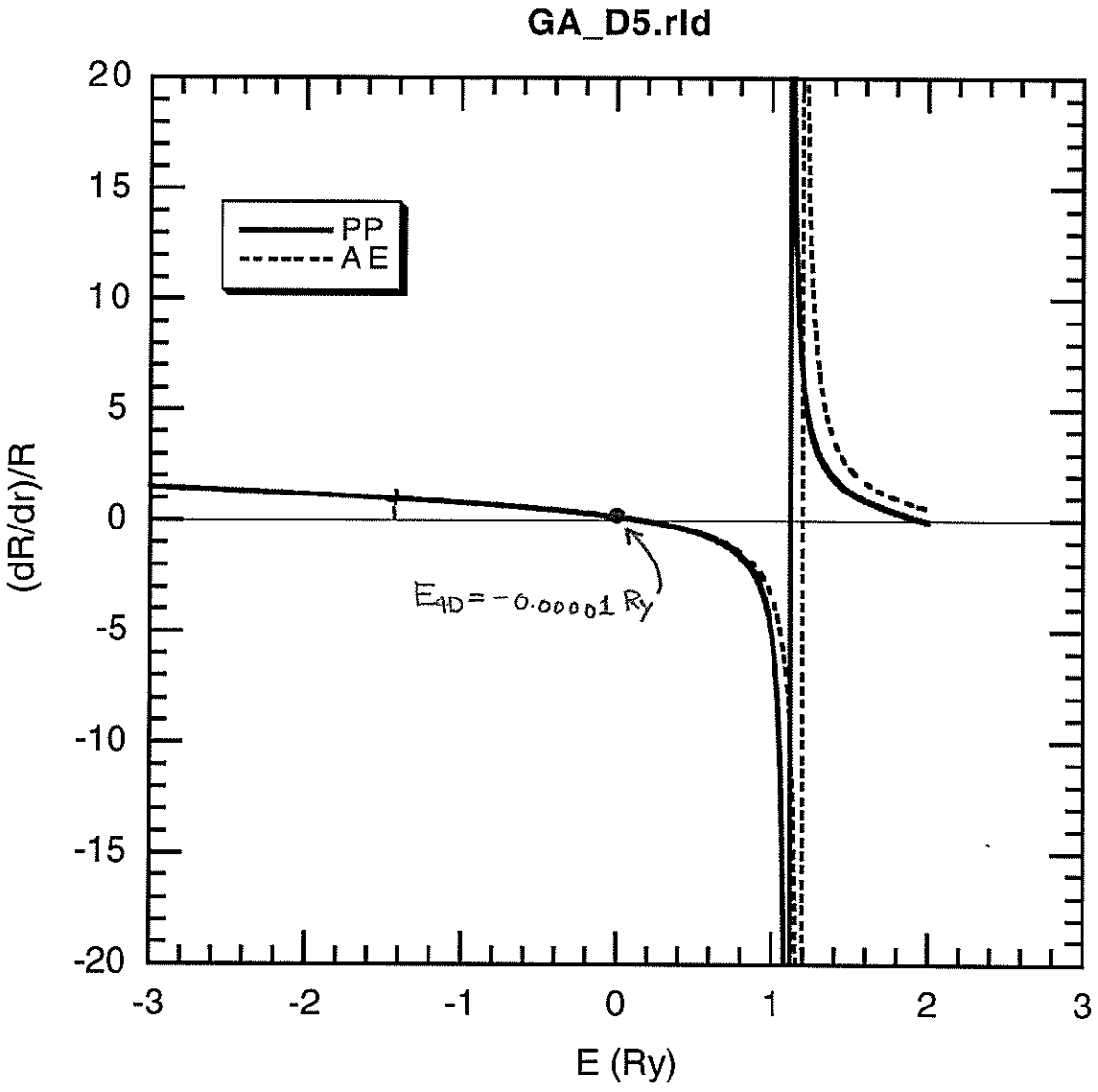

GA_S1.rld
PP
AE
$E_{4S} = -0.6731$ Ry
(dR/dr)/R
E (Ry)
20
15
10
5
0
-5
-10
-15
-20
-3
-2
-1
0
1
2
3


GA_P3.rld
PP
AE
$E_{AP} = -0.2014$ Ry
(dR/dr)/R
E (Ry)
20
15
10
5
0
-5
-10
-15
-20
-3
-2
-1
0
1
2
3


GA_D5.rld
PP
AE
$E_{4D} = -0.00001$ Ry
(dR/dr)/R
E (Ry)
20
15
10
5
0
-5
-10
-15
-20
-3
-2
-1
0
1
2
3

— Design

1. Construct pseudowavefunctions to satisfy requirements, 1-4. (See below.)

2. Obtain screened pseudopotentials by inverting the radial Schrödinger equation,

$$\left[-\frac{d^2}{dr^2} + V^{PP}_{scr,\ell}(r) + \frac{\ell(\ell+1)}{r^2} - E_\ell\right]\left[r R^{PP}_\ell(r)\right] = 0 \qquad (6)$$

(We use Bohr-Rydberg unit.)

or

$$V^{PP}_{scr,\ell}(r) = E_\ell - \frac{\ell(\ell+1)}{r^2} + \frac{1}{r R^{PP}_\ell(r)} \frac{d^2}{dr^2}\left[r R^{PP}_\ell(r)\right] \qquad (7)$$

Since $R^{PP}_\ell(r)$ is nodeless, there is no singularity in this potential. (Singularity at the origin is considered below.)

3. Consider a z (= valence-electron number = 3 for Ga) electron, self-consistent problem,

$$\left[-\frac{d^2}{dr^2} + V^{PP}_{ion,\ell}(r) + V^{PP}_H(r) + V^{PP}_{xc}(r)\right] r R^{PP}_\ell(r) = E_\ell\, r R^{PP}_\ell(r) \qquad (8)$$

$$V_H(r) = \int d\vec{r}\,' \frac{2\rho(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} \qquad (9)$$

$$V_{xc}(r) = \mu_{xc}(\rho(r)) \qquad (10)$$

$$\rho(r) = \sum_{\ell=0}^{2} w_\ell \left|R^{PP}_\ell(r)\right|^2$$

(w_ℓ: occupation ($w_0 = 2$, $w_1 = 1$, $w_2 = 0$ for Ga))

In order for this z-electron problem to produce $R^{PP}_\ell(r)$ to be the ground state,

$$V^{PP}_{ion,\ell}(r) \equiv V^{PP}_{scr,\ell}(r) - V^{PP}_H(r) - V^{PP}_{xc}(r) \qquad (11)$$

Note that $V^{PP}_{scr,l}(r)$ is completely screened out (exponentially decaying) for $r \to \infty$. (Note that no self-interaction is corrected in LDA.)

In contrary, $V^{PP}_{ion,l}(r)$, after subtracting $V_H(r)$ from $\bar{z}$ atoms asymptotically behaves

$$V^{PP}_{ion,l}(r) \longrightarrow -\frac{2\bar{z}}{r} \qquad (12)$$

2 : Rydberg, $\bar{z}$: valence number