Density functional theory
plane-wave/pseudopotential calculations of the
equation of state of rhenium in the terapascal regime

G L Rech, and C A Perottoni*
Universidade de Caxias do Sul, 95070-560 Caxias do Sul – RS, Brazil
E-mail: *caperott@ucs.br

Abstract.
The equation of state (EOS) of hexagonal close-packed rhenium has been previously
determined up to 1.5 TPa (V/V₀ = 0.46) using all-electron (AE) density functional theory
(DFT) including core relativistic effects [Phys. Rev. B 100, 174107 (2019)]. This work focuses
on assessing the validity of pseudopotentials at such high-pressures, above 1 terapascal (TPa),
by comparing the EOS obtained using plane-wave/pseudopotentials (PW/PPs) with previous
AE calculations. Both ONCV pseudopotentials tested (PBE and PBEsol) yield results in good
agreement with all-electron calculations. The fitted parameters of the Rose-Vinet EOS, the
bulk modulus, B₀ (380(2) GPa and 379(3) GPa for the PBE and PBEsol PPs), and its pressure
derivative, B₀’ (4.58(2) and 4.59(3) for the PBE and PBEsol PPs), are in good agreement with
previous all-electron results (B₀=367(5) GPa and B₀’=4.64(3)). The agreement is worse for the
equilibrium volume at zero pressure, V₀ (199.9(2) Bohr³ and 199.2(2) Bohr³ for PBE and PBEsol
PPs, versus 196.7(3) Bohr³ for AE). Even so, for a given V/V₀ ratio, the pressures estimated
using the EOS derived from the PPs and AE calculations are in very good agreement, thus
suggesting that the PPs used in this study are valid even at such high compression regime.

1. Introduction
Rhenium is a rare transition element which, owing to its high melting point and strength increase
under plastic deformation, is well suited to be used as a metal gasket in high-pressure experiments
with the diamond-anvil cell [1; 2]. In these experiments, particularly at very high pressures, the
gasket itself can be used to estimate the pressure by x-ray diffraction at the point of contact
with the sample. The pressure is then obtained from the equation of state (EOS) of the gasket’s
material [3]. All electron (AE) density function theory have been previously used to determine de
EOS of rhenium for compressions down to V/V₀=0.46 [4]. As a less computationally demanding
alternative, one may use pseudopotentials for DFT simulations. However, in this case, pitfalls
due to core overlap at very high pressures may be a source of concern [5]. This work aims to check
how well two Optimized Norm-Conserving Vanderbilt (ONCV) pseudopotentials reproduce the
EOS obtained from previous AE calculations[4].

2. Methodology
All the density functional theory pseudopotential calculations were performed using Quantum
Espresso [6]. Two ONCV fully relativistic pseudopotentials were used, the first one built for
the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional [7; 8], and the second one for the PBE functional optimized for solids (PBEsol) [7; 9]. Both PPs consider 5s24p65d6s2 spin-polarized valence electrons. The calculations were performed using a kinetic energy cutoff of 75 Ha in the plane-wave expansion of the wavefunction, a charge-density cutoff of 300 Ha and a 31×31×19 Monkhorst-Pack k-point grid. The tolerance in the self-consistent field calculations was 0.05 µHa/atom. These conditions were chosen to ensure a convergence in total energy within 5 µHa/atom. All calculation parameters were chosen to reproduce, where applicable, the same conditions of the previous all-electron calculations [4].

Total energy versus c/a curves were calculated for several unit-cell volumes, from which the minimum of a fitted second-degree polynomial was taken as the equilibrium energy and c/a ratio for each volume. The isothermal Vinet EOS,

\[ E(V) = E(V_0) + \frac{9B_0V_0}{\eta^2} [1 + e^{\eta x}(\eta x - 1)] \]

where \( x = 1 - (V/V_0)^{1/3} \) and \( \eta = \frac{3}{2} (B'_0 - 1) \), was fitted to the energy versus volume curve to yield rhenium’s equilibrium volume at zero pressure \( V_0 \), bulk modulus \( B_0 \), and its pressure derivative \( B'_0 \). The input and some relevant output files were deposited in the NoMaD repository [10].

3. Results

A comparison of total energy versus unit cell volume, as obtained from pseudopotential and all-electron calculations, is presented in Figure 1. Though small, the difference in energy between PP and AE increases with increasing compression. For the highest compression simulated, the PP approach using PBE overestimate the total energy by about 1.40 Ha, when compared to AE.

The c/a ratio together with the fitted parameters of the Rose-Vinet EOS for each of the approaches is presented in Table 1. The results differ mostly for the equilibrium volume at zero pressure, \( V_0 \). Figure 2 represents the three EOS for rhenium.

**Figure 1.** Total energy w.r.t. equilibrium energy versus unit cell volume for rhenium, in the athermal limit. Continuous lines represent the Vinet EOS fitted to data. The inset shows an expanded view around the point of minimum energy.

**Figure 2.** Volume versus pressure for rhenium in the athermal limit. Pressure was estimated using the Vinet EOS (represented by the continuous lines) with the parameters given in Table 1.
Table 1. Rhenium’s zero pressure unit cell volume, c/a ratio, bulk modulus and its first pressure derivative, as obtained by fitting of the Vinet equation of state to total energy versus unit cell volume data.

| Parameter | ONCV PBE | ONCV PBEsol | All-electron |
|-----------|----------|-------------|--------------|
| $V_0$ (Bohr$^3$) | 199.9(2) | 199.2(2) | 196.7(3) |
| c/a | 1.6154 | 1.6149 | 1.6125(3) |
| $B_0$ (GPa) | 380(2) | 379(3) | 367(5) |
| $B_0’$ | 4.58(2) | 4.59(2) | 4.64(3) |

The non-monotonic dependence of the c/a ratio with pressure previously reported in the AE study was also observed in the PP results, though with a shifted minimum to higher pressures from about 0.4 TPa in AE calculations to about 0.6 TPa in both pseudopotentials calculations, as seen in Figure 3.

Figure 3. Dependence of the c/a ratio of rhenium on pressure and volume (in the inset). The solid lines in the inset represents fifth-degree polynomia fitted to data. The continuous line in the main panel was obtained from the polynomial expression for c/a as a function of volume, which was converted into a pressure scale with the fitted Vinet EOS for each method.

4. Conclusion
The Optimized Norm-Conserving Vanderbilt pseudopotentials were built to reproduce all-electron calculations. The difference in the energy calculated using PPs and all-electron increases smoothly with increasing pressure, but even for the highest compression regime studied ($V/V_0=0.46$), the EOS obtained from PPs show reasonable agreement with the EOS obtained using AE calculations. The bulk modulus and its pressure derivative from ONCV PP calculations are in good agreement with AE results. For a given $V/V_0$ ratio, the pressures estimated using the EOS derived from the PPs and AE calculations are in very good agreement, thus suggesting that the PPs used in this study allow obtaining a $V/V_0$ versus pressure relation almost indistinguishable from AE calculations even at the high compression regime.
References

[1] Eremets M 1996 *High pressure experimental methods* (Oxford University Press)

[2] Schiferl D 1987 *Review of scientific instruments* **58** 1316–1317

[3] Anzellini S, Dewaele A, Occelli F, Loubeyre P and Mezouar M 2014 *Journal of Applied Physics* **115** 043511

[4] Rech G, Zorzi J and Perottoni C 2019 *Physical Review B* **100** 174107

[5] Winkler B and Milman V 2014 *Zeitschrift für Kristallographie–Crystalline Materials* **229** 112–122

[6] Giannozzi P, Andreussi O, Brumme T, Bunau O, Nardelli M B, Calandra M, Car R, Cavazzoni C, Ceresoli D, Cococcioni M, Colonna N, Carnimeo I, Corso A D, de Gironcoli S, Delugas P, Jr R A D, Ferretti A, Floris A, Fratesi G, Fugallo G, Gebauer R, Gerstmann U, Giustino F, Gorni T, Jia J, Kawamura M, Ko H Y, Kokalj A, Küçükbenli E, Lazzeri M, Marsili M, Marzari N, Mauri F, Nguyen N L, Nguyen H V, de-la Roza A O, Paulatto L, Poncé S, Rocca D, Sabatini R, Santra B, Schlipf M, Seitsonen A P, Smogunov A, Timrov I, Thonhauser T, Umari P, Vast N, Wu X and Baroni S 2017 *J. Phys.-Condens. Mat.* **29** 465901

[7] Hamann D R 2013 *Phys. Rev. B* **88**(8) 085117

[8] Scherpelz P, Govoni M, Hamada I and Galli G 2016 *J. Chem. Theory Comput.* **12** 3523–3544

[9] Van Setten M, Giantomassi M, Bousquet E, Verstraete M J, Hamann D R, Gonze X and Rignanese G M 2018 *Comput. Phys. Commun.* **226** 39–54

[10] 2019 QUANTUM ESPRESSO input and output files [Accessed: 28-Feb-2020]