

# Simplified pseudopotential problems for the classroom

T. Salagaram, R. C. Andrew, and N. Chetty

**Abstract**—*Ab initio* methods have been used for many decades to accurately predict properties of solids such as the physical, electronic, optical, magnetic, and elastic properties. A generation ago, many research groups developed their own in-house codes to perform *ab initio* calculations. In doing so, research students were intimately involved in many aspects of the coding, such as developing the theoretical framework, and algorithmic and programming details. Over time however, collaborations between various research groups within academia and in industry have resulted in the creation of more than 50 large open-source and commercial electronic structure packages. These software packages are widely used today for condensed matter research by students who, unfortunately, often have very little understanding of the fundamental aspects of these codes. To address this shortcoming, we have embarked on a program at the University of Pretoria to devise a range of simplified, easily programmable computational problems appropriate for the classroom, which can be used to teach advanced undergraduate students about particular theoretical and computational aspects of the electronic structure method. In this paper, we focus on the pseudopotential, which is a centrally important concept in many modern *ab initio* methods. Whereas the full implementation of the pseudopotential construct in a real electronic structure code requires complex numerical methods, e.g. accelerated convergence to self-consistency including the interactions between all the electrons in the system, we show that the essential principles of the pseudopotential can, nevertheless, be presented in a simpler class of problems, which can readily be coded by students.

**Index Terms**—pseudopotentials, 1-dimensional, DFT, computational methods



## 1 INTRODUCTION

The 1964 paper by Hohenberg and Kohn on Density Functional Theory (DFT)[1] and many of the publications describing the key approximations related to the implementation of DFT[2], [3], [4] are among the most cited physics papers of all time. The number of citations for these fundamental papers in DFT is set to grow because of the increasing number of scientists across many different scientific and engineering disciplines that are using DFT codes in their research today.

In the 80's, researchers often developed their own density functional codes and many graduate students were intimately involved in all aspects of code development. The situation today cannot be more different. We have access to very slick commercial codes and even some excellent academic codes that are highly automated and optimized to run on some of the fastest and highly parallel computing architectures. These codes are written by teams of dedicated professionals whose job it is to automate these

highly versatile codes for the growing community of practitioners. The practitioner has nothing more to do than choose from pull-down menus and then to turn the proverbial computational knobs to launch computations that were simply not possible barely a decade ago. Consequently, we are producing students who are very adept at utilizing computational code in their applications to real physical systems, but the vast majority have no inkling about the details of the algorithms for key components of these codes and the theoretical framework that underpin these components.

These students do not develop the necessary computational skills that make them transferable to different scientific working environments, and this should be a worry for any educator. We fear that this problem is true of other computational communities as well, e.g. computational astrophysics, computational fluid dynamics, and so on.

Our aim is to develop computational projects in electronic structure methods that attempt to address these shortcomings, *albeit* at a fairly basic level appropriate to advanced undergraduate studies. In Fig. 1 the key steps in the self-consistent solutions of the Kohn-Sham equations are shown. The challenge for us is to develop problems that are "stand-alone" problems which only focus on the essential physics and computing aspects of Fig 1.

For example, pseudopotentials are generated in 3 dimensions, in the context of self-consistency involving many interacting electrons and particular choices for the exchange-correlation functionals. Pseudopo-

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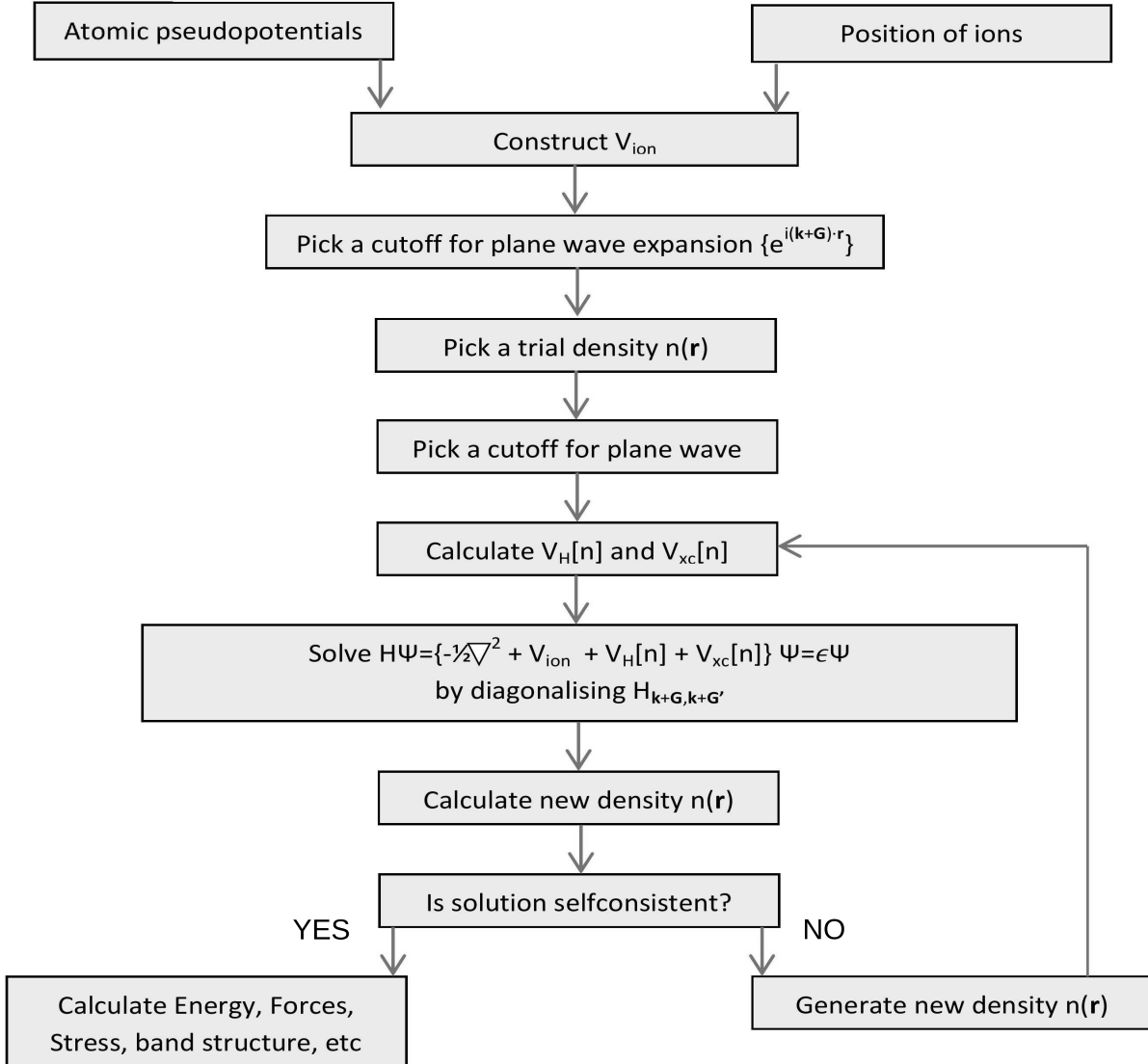


Fig. 1: Self-consistent solution of the Kohn-Sham equations within the plane-wave pseudopotential method.

tentials were first used in neutron scattering[5] and atomic physics[6], [8] to simplify complex problems. The essential idea of the pseudopotential can be stripped down to a very small subset of constructs that may be easily implemented in one dimensional quantum mechanical problems such as the harmonic oscillator. In this way, we see the problems that we are developing as mimicking particular key aspects of real electronic structure codes.

In this paper, we focus on developing simplified pseudopotential problems for the classroom. Specifically, we are focusing on the so-called *ab initio* pseudopotentials as different from the so-called empirical pseudopotentials[7], [8], [9]. We believe that the

advanced undergraduate student working through a range of problems of this nature develops a good pedagogical understanding of this key aspect of the plane wave pseudopotential method. There are other basis sets that one can use to represent the electronic energy states of a solid state system such as localised atomic orbitals, etc. However, plane waves are simplest, elegant and pedagogical, and appropriate for developing the concept of the pseudopotential in the classroom.

## 2 CREATING NORM CONSERVING PSEUDOPOTENTIALS FOR 1-D SYSTEMS

In real atomic systems, the interaction between valence electrons and the stationary ions cause the high level valence electron wavefunctions to oscillate rapidly in the core region. This makes a numerical study of a solid state system difficult as it requires a great many plane waves to accurately represent this rapid oscillatory behavior. One way in which this may be overcome is by replacing the actual Coulombic potential with a suitable pseudopotential which accurately describes the interaction between the ionic core and valence electrons, and which makes a numerical solution easier because the pseudo wavefunction is smoother.

The implementation of the pseudopotential method in atomic systems is rather intricate. However the essential principles can be captured in a simpler class of problems. In this paper, we create norm conserving pseudopotentials for simple, non-interacting 1-D systems, such as the infinite square well (ISW), finite square well (FSW), simple harmonic oscillator (SHO) and the radial solution of the 3-D hydrogen atom (only one electron so the complications that arise from including many-electron interactions do not apply)[10], to illustrate the pseudopotential method.

There are several ways of creating pseudopotentials[11], [12], [13], [14]. In this paper we focus on the method used by G.P. Kerker[12]. The first step in creating a norm conserving pseudopotential (NCP) is to create a pseudo wavefunction,  $F(x)$ , for a chosen quantum state,  $n$ , of the system being studied. The pseudo wavefunction is constructed to be nodeless for even parity solutions, and to have a single node for odd parity solutions for ISW, FSW and SHO. For the radial solution of hydrogen, the pseudo wavefunction is constructed to be nodeless. For all the 1-D systems considered, except hydrogen, this is accomplished by first choosing two cut-off lengths,  $-x_c$  and  $x_c$ , that lie between the first and last maximum of the actual wavefunction  $\Psi(x)$ . This preserves the symmetry of the system. The pseudo wavefunction is then created by interpolating between  $-x_c$  and  $x_c$ . The interpolation may be numerical, or one may use an analytical function such as a polynomial, exponential, Gaussian, etc. For  $x \leq -x_c$  and  $x \geq x_c$ , the pseudo wavefunction exactly coincides with the actual wavefunction. We choose the following interpolating function for the ISW, FSW and SHO,

$$F(x) = x^\eta \exp(ax^6 + bx^4 + cx^2 + d), \quad (1)$$

to create norm conserving pseudo wavefunctions for these 1-D systems.

Since the potentials for these systems are symmetric even functions of  $x$ , the wavefunctions have either

even or odd parity. We tailor a pseudo wavefunction for an even or odd state such that it resembles the ground state for the respective even or odd case. Therefore a pseudo wavefunction for an even state will be nodeless, whereas that for an odd state will consist of one node. The exponent  $\eta$  in (1) is equal to 0 for the even states and 1 for the odd states of ISW, FSW and the SHO.

For the hydrogen atom, a nodeless pseudo wavefunction is obtained by interpolating from  $x = 0$  to a single cut-off radius  $x_c$  which lies between the last node and maximum of the real wavefunction. The interpolating function used is

$$F(x) = x^\eta \exp(ax^4 + bx^3 + cx^2 + d), \quad (2)$$

where  $\eta$  is equal to  $(l + 1)$  where  $l$  is the angular momentum quantum number. This is in keeping with Kerker's method for atomic systems[12].

The constants  $a$ ,  $b$ ,  $c$  and  $d$  in (1) and (2) are determined by applying the following constraints:

- 1) the pseudo wavefunction is equal to the real wavefunction at  $x_c$ :

$$F(x_c) = \Psi(x_c), \quad (3)$$

- 2) the first and second derivatives of the pseudo wavefunction are equal to those of the real wavefunction at  $x_c$ :

$$F'(x_c) = \Psi'(x_c), \quad (4)$$

$$F''(x_c) = \Psi''(x_c), \quad (5)$$

- 3) the real and pseudo system have the same eigenvalue for the quantum state  $n$  being pseudized:

$$\epsilon_{ps} = \epsilon_n, \quad (6)$$

- 4) and the norm of the real and pseudo system within the pseudized range is conserved:

$$\int_{-x_c}^{x_c} |F(x)|^2 dx = \int_{-x_c}^{x_c} |\Psi(x)|^2 dx, \quad (7)$$

with

$$\int_0^{x_c} |F(x)|^2 dx = \int_0^{x_c} |\Psi(x)|^2 dx. \quad (8)$$

for hydrogen.

For the ISW, FSW and SHO (3) to (5) at  $-x_c$  are satisfied by symmetry. For the hydrogen atom the cut-off region is  $0 \leq x \leq x_c$  and the conditions are satisfied at  $x_c$ .

The cut-off region referred to thus far is the region where the wavefunction is relegated nodeless subject to norm conservation, and beyond which there is no change to the wavefunction. This mimics the situation in real chemical systems where the tail end of the wavefunctions participate in chemical bonding, but the core remains essentially inert.

The pseudopotential,  $V_{ps}$ , is determined by inverting the 1-D Schrödinger equation for the pseudo system, which in terms of Rydberg atomic units where  $\hbar/2m = 1$ , is given by

$$-F''(x) + V_{ps}(x)F(x) = \epsilon_n F(x). \quad (9)$$

This yields:

$$V_{ps}(x) = \epsilon_n + \frac{F''(x)}{F(x)}. \quad (10)$$

$F(x)$  is deliberately chosen so that the term  $F''/F$  in (10) is finite for all  $x$  including at  $x = 0$  where  $F(0) = 0$ .

The conditions (7) or (8) ensures that the pseudo wavefunction is properly normalized. It also ensures that the norm of the real and pseudo system are the same between  $-x_c$  and  $x_c$  (0 and  $x_c$  for hydrogen), and consequently the scattering properties of the core of the real potential are transferred to that of the pseudopotential. The scattering phase shifts of quantum systems are related to the first energy derivative of the logarithmic derivative of the wavefunction[15]. Therefore the transferability of a pseudopotential can be determined by plotting the logarithmic derivative of the pseudo wavefunction as a function of energy and comparing this to that of the real wavefunction. This is done numerically by integrating the discrete version of the Schrödinger equation for the pseudo system

$$-\left[ \frac{F_{i+1} - 2F_i + F_{i-1}}{(\Delta x)^2} \right] + V_{ps}^i F_i = E F_i,$$

to calculate the wavefunction  $F_{i+1}$  over a range of energies  $E$ ,

$$F_{i+1} = (V_{ps}^i - E) \Delta x^2 F_i + 2F_i - F_{i-1}, \quad (11)$$

where  $i$  is the index for the spatial grid and  $\epsilon_n - \delta < E < \epsilon_n + \delta$ . Thereafter the logarithmic derivative of the wavefunction at a particular diagnostic length  $x_D$  is calculated using the following finite difference expression:

$$x_D \frac{d}{dx} \ln F|_{x_D} = \frac{x_D (F_{i_D+1} - F_{i_D-1})}{F_{i_D} (2 \Delta x)}, \quad (12)$$

where  $i_D$  is the spatial index of the diagnostic length  $x_D$ . In this study we have chosen  $x_D = x_c$ . Similar equations are used to calculate the logarithmic derivative of the real wavefunction. The energy range for which these curves coincide for the real and pseudo wavefunctions is a direct measure of the range of energies for which the pseudopotential is transferable[15]. In a solid, the atomic energy levels spread into bands of energies, and so norm conservation ultimately guarantees that the single particle states in a solid are accurately determined within the pseudopotential framework.

### 3 RESULTS AND DISCUSSION

#### 3.1 Infinite square well, finite square well and simple harmonic oscillator

Real wavefunctions for the second and third excited states for the ISW and the corresponding pseudo wavefunctions are presented in Fig. 2a and Fig. 2d, respectively. The pseudo wavefunctions are obtained by satisfying conditions (3)-(7). The pseudo wavefunction of the second excited state is nodeless, smooth and continuous with the real wavefunction in the cut-off region, as desired. The pseudo wavefunction of the third excited state has a single node at the origin as desired, and is also smooth and continuous with the real wavefunction in the interpolated interval. These results illustrate that the chosen interpolating function (1) is a suitable one for the ISW.

The corresponding pseudopotentials are calculated using (10). These are plotted together with the real potentials in Fig. 2b for the second excited state and Fig. 2e for the third excited state of the ISW. The pseudopotentials are equal to the actual potentials for  $x \leq -x_c$  and  $x \geq x_c$ . The transferability of these pseudopotentials is determined by comparing the logarithmic derivatives of the real and pseudo wavefunctions as a function of energy. These results are presented in Fig. 2c and Fig. 2f for the second and third excited states of the ISW, respectively.

For the second excited state the transferability of the pseudopotential appears to be reasonable as the logarithmic derivatives show observable deviation around the energy level of interest, as indicated by the arrow in Fig. 2c. To clarify this result an ancillary test, which involves comparing the eigen energy of the fourth excited state of the real ISW potential with the first excited state of the pseudopotential, is performed. These energies differ by more than 10% which suggests that more work has to be done to improve on the interpolation scheme to derive a more transferable potential. This is also exemplified in Fig. 2f where in the case of the third excited state, the logarithmic derivatives show significant deviation around the energy level of interest. We leave it to the reader to explore improved interpolation schemes to increase the transferability of the potential.

Similar results are obtained for the FSW (Fig. 3) and SHO (Fig. 4), where (1) is used to create a pseudo wavefunction for the second excited state of both these systems. The corresponding pseudopotentials obtained using (10) are not transferable to other excited eigenstates, as there are significant deviations between the logarithmic derivatives for the real and pseudo wavefunctions (in Fig. 3c and Fig. 4c) around the energy levels of interest.

#### 3.2 Hydrogen

Nodeless pseudo wavefunctions for the  $2s$ ,  $3p$  and  $4d$  states of hydrogen are obtained using the inter-

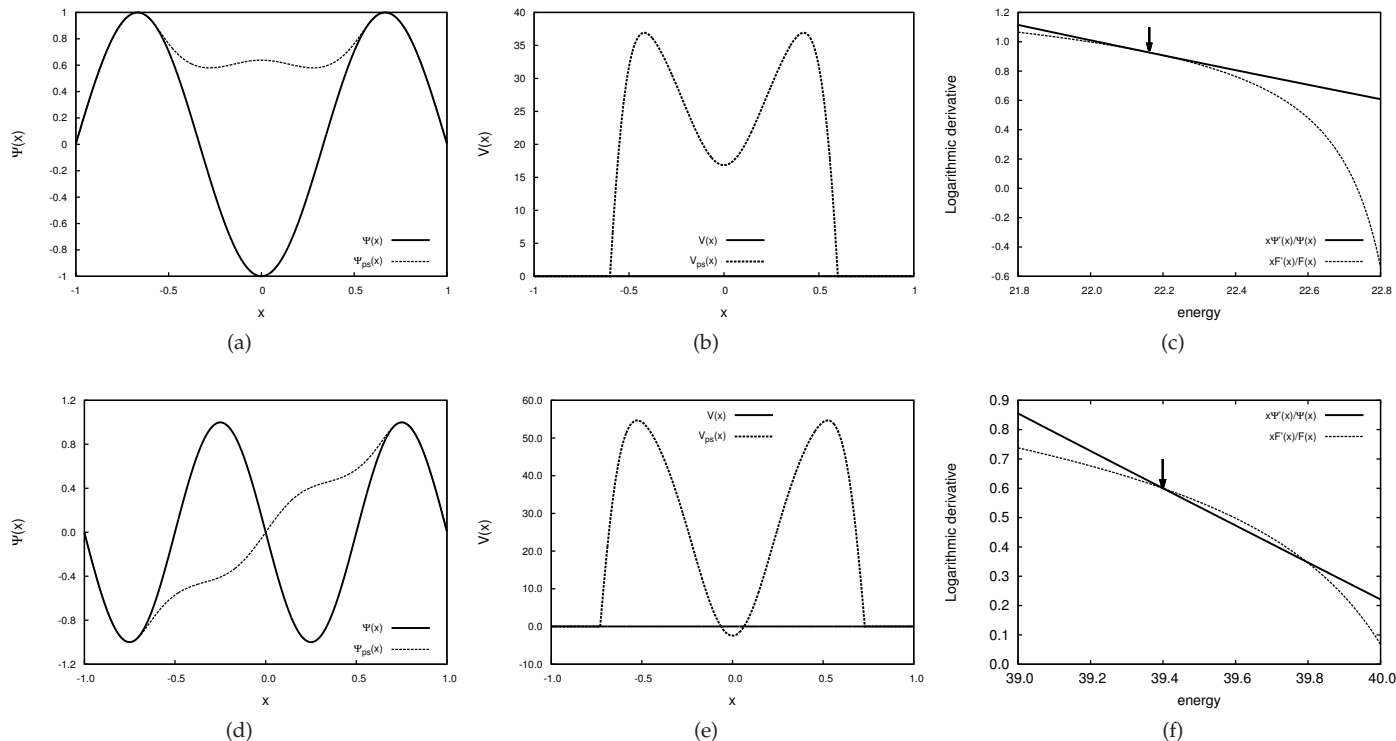


Fig. 2: Wavefunctions, potentials and logarithmic derivatives for the real (solid line) and pseudo (dashed line) infinite square well (ISW). The top row consists of results for the second excited state of the ISW which is an even parity state, and the bottom row consists results for the third excited state of the ISW which is an odd parity state.

polating function (2) which has to satisfy conditions (3)-(6) and (8). These are presented in the first row of Fig. 5. The pseudopotentials are plotted together with the real potentials in the second row of Fig. 5. These are finite at the origin, which is a desirable feature, especially in the computational study of more complex solid state systems, as it reduces the number of plane waves required to accurately describe the system.

The logarithmic derivatives of the real and pseudo wavefunctions versus energy are presented in the third row of Fig. 5. The result for the  $2s$  state show excellent tracking of the curves for the logarithmic derivatives of the real and pseudo wavefunctions over a wide energy range. The energies of the first excited state of the pseudopotential and the  $n = 3$  excited state differ by less than 1%. This is indicative of a highly transferable pseudopotential to more complex chemical environments[13], [15] involving hydrogen. The pseudopotential has a repulsive core which simply reflects the repulsion due to the Pauli exclusion principle (orthonormality of the states in this context means that the higher level states for a given orbital momentum quantum number are ‘pushed’ out). The results obtained for the  $3p$  and  $4d$  states of hydrogen are reasonable, however they suggest that the transferability of pseudopotential decreases as the energy

of the state increases.

Other interpolating functions may be used to create nodeless pseudo wavefunctions to obtain more transferable pseudopotentials which makes for useful exercises for students.

## 4 CONCLUSIONS

We created norm conserving pseudopotentials for several non-interacting 1-D quantum mechanical systems. The purpose of this endeavor was to develop computational exercises to teach undergraduate and graduate students particular theoretical and numerical aspects of the pseudopotential method which is an essential aspect of modern *ab initio* codes and which many graduate students do not understand, in spite of them using these *ab initio* codes for their research. The construction of a nodeless pseudo wavefunction by interpolation, calculation of the pseudopotential by numerically inverting the Schrödinger equation and how to determine the transferability of the pseudopotential from the logarithmic derivatives of the real and pseudo wavefunctions versus energy, were aspects covered in this paper.

We applied the method described in G. P. Kerker’s paper[12] to calculate norm conserving pseudopotentials for the ISW, FSW, SHO and the hydrogen atom. The chosen interpolating functions, namely, (1)

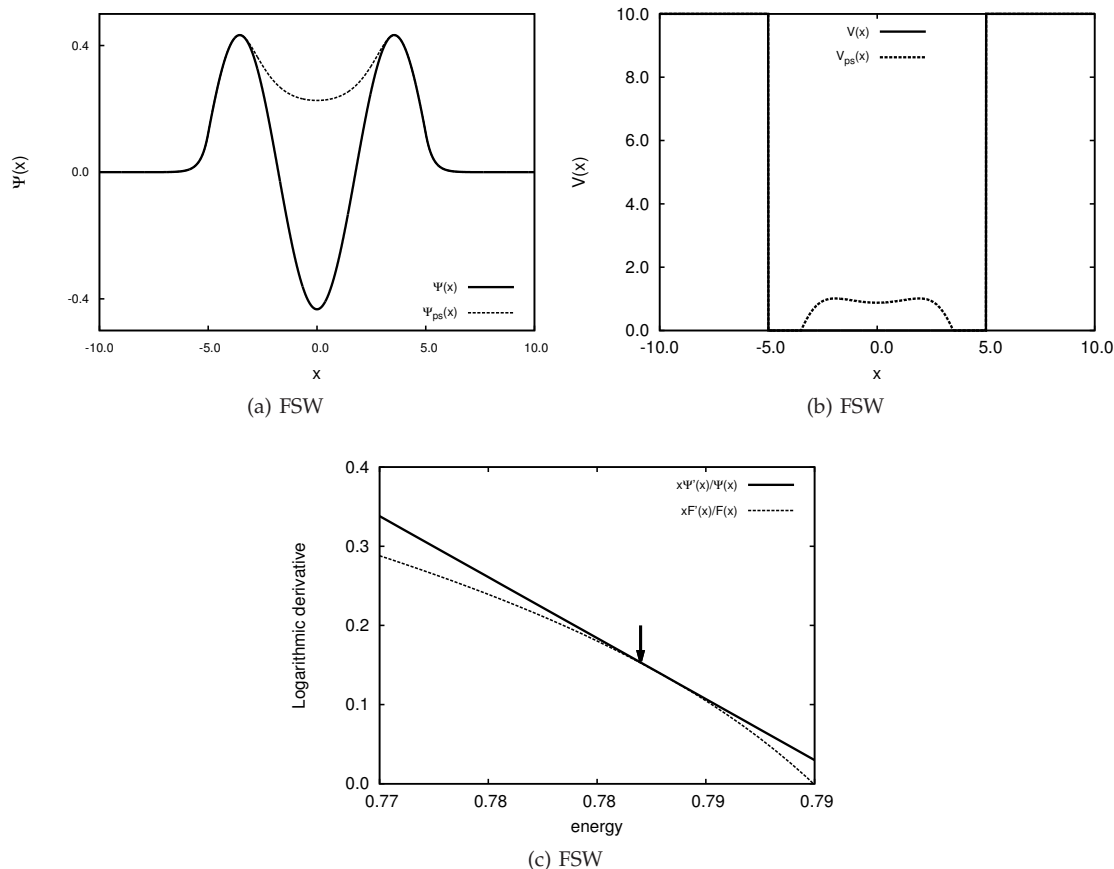


Fig. 3: Wavefunctions, potentials and logarithmic derivatives for the real (solid line) and pseudo (dashed line) finite square well (FSW). The second excited state for this system is pseudized.

for ISW, FSW and SHO, and (2) for hydrogen, yield nodeless wavefunctions for all the systems, as desired. The logarithmic derivative of the real wavefunction and the pseudo wavefunction were compared to determine the transferability of the calculated pseudopotentials to higher energy levels (in the case of the ISW, FSW and SHO) or to more complex chemical systems (in the case of the hydrogen atom). A highly transferable pseudopotential was obtained for the  $2s$  state of the hydrogen atom, reasonably transferable pseudopotentials were obtained for the third excited state of the ISW, the  $3p$  and  $4d$  state of the hydrogen atom, and untransferable pseudopotentials were obtained for the other systems studied.

These exercises are simple and require reasonably uncomplicated algorithms to produce a working numerical solution. However a student will have to thoroughly understand all aspects (theoretical, numerical and programming) of the problem to produce a correct numerical solution. Therefore such exercises can be used to enhance students understanding of the pseudopotential method.

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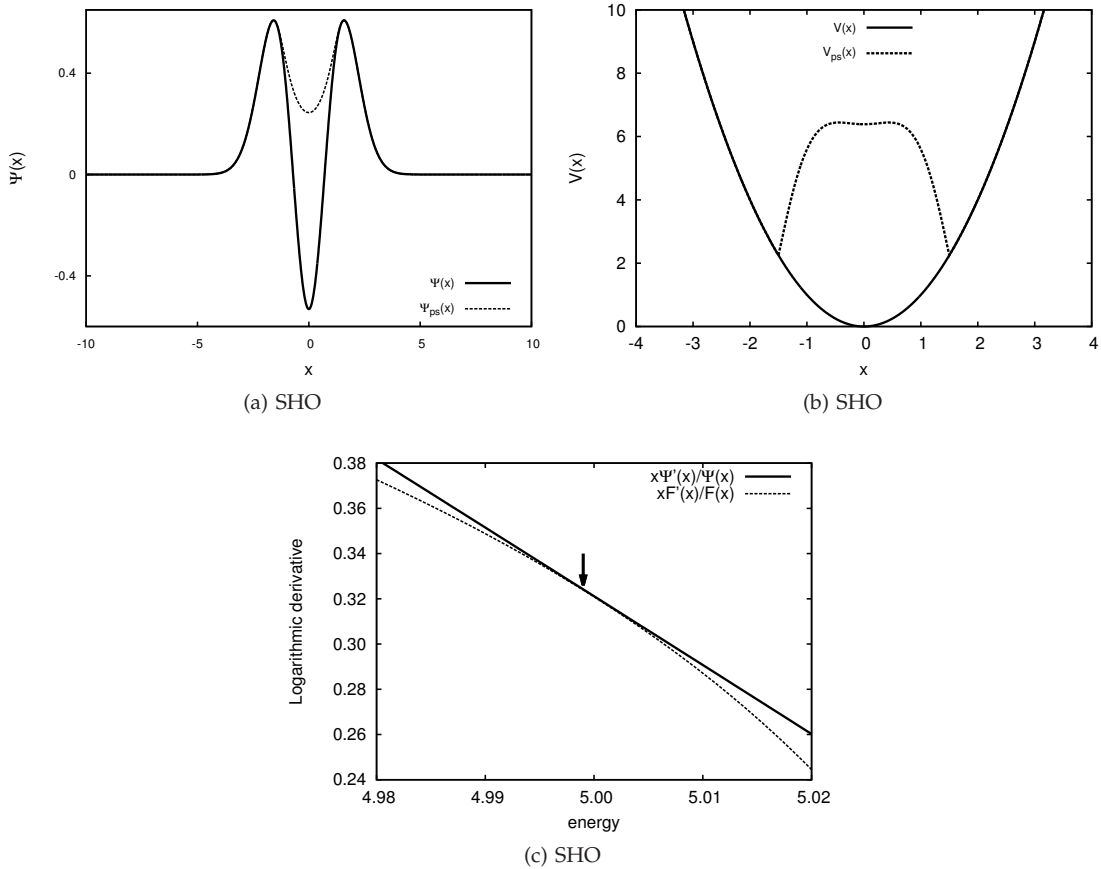


Fig. 4: Wavefunctions, potentials and logarithmic derivatives for the real (solid line) and pseudo (dashed line) simple harmonic oscillator (SHO). The second excited state is pseudized.

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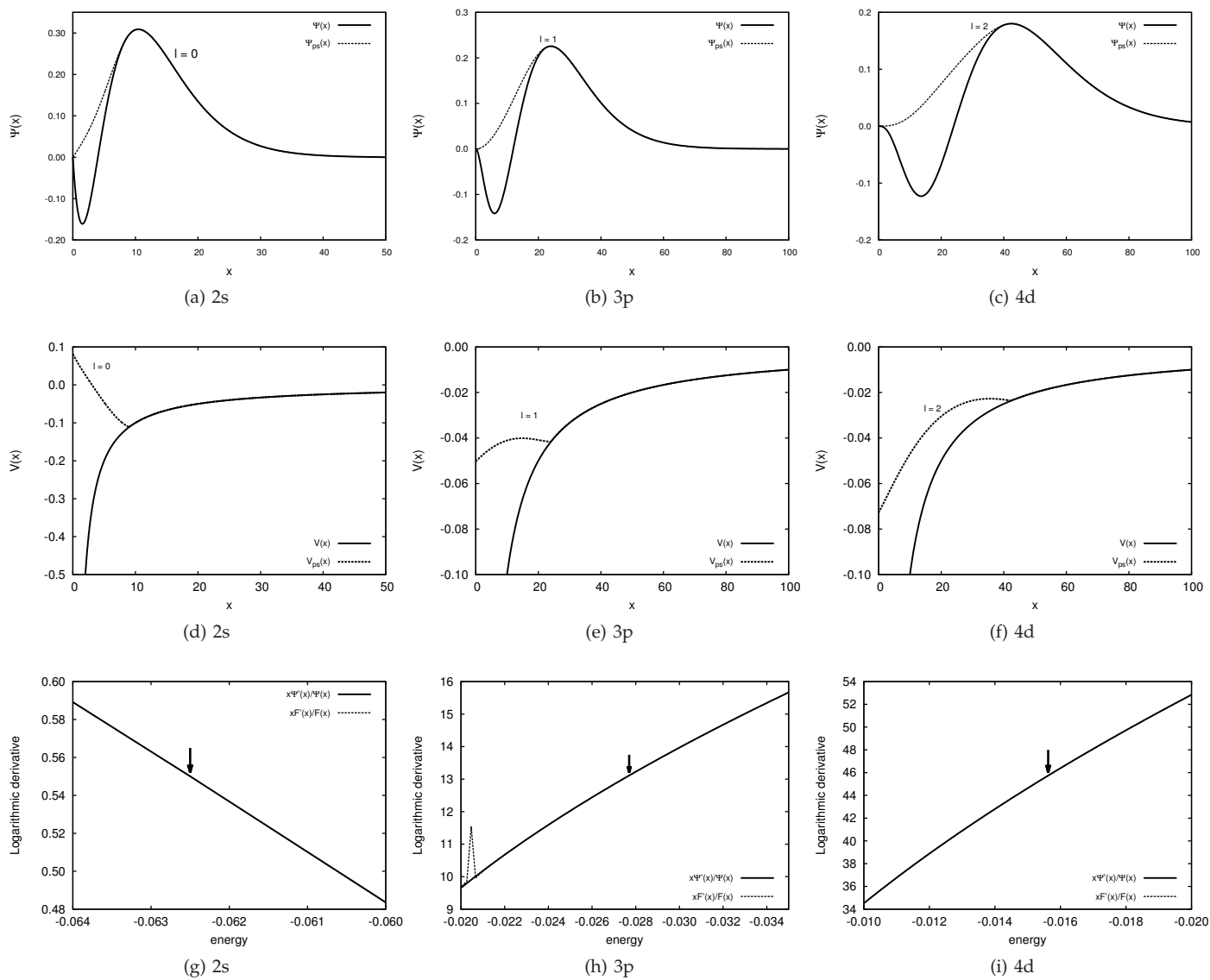


Fig. 5: Wavefunctions, potentials and logarithmic derivatives for the real (solid line) and pseudo (dashed line) hydrogen atom. The 2s, 3p and 4d states are pseudized.