

Model Pseudopotentials as a Source of Useful Problems for Quantum Chemistry Courses

Teaching courses in quantum chemistry year after year one can become jaded by the use of the same problems over and over again in assignments and examinations. In addition, the existence of compendia of problems and solutions such as that of Johnson and Pederson (1), as valuable as they are, lead some students into making assignments into library projects, thus subverting their usefulness in training and evaluating the student. Although many of the old problems cannot be discarded because of their importance to the subject, it is clearly desirable to have an influx of new problems to mix with the old ones.

Any new problem has a certain intrinsic value no matter how remote from real physical application; I would love to be able to assign the problem of a particle constrained to move on the surface of a Moebius strip or a Klein bottle. However, to be most useful problems should satisfy the following criteria

- 1) They should illustrate and illuminate the principles and methods of quantum mechanics.
- 2) They should be tractable to students of moderate mathematical sophistication.
- 3) They should have physically meaningful content in the sense that they should deal with quantities that can be compared with values measured in the laboratory.
- 4) They should broaden as well as deepen the students' knowledge.

In the course of some research involving model pseudopotentials, the author was impressed by the possibilities offered by model pseudopotentials as a source of problems which are not contained in current texts and compendia and which satisfy the criteria listed above. The object of this paper is to present some problems based upon model pseudopotentials (mostly the Simons Model Potential (2)) and to include some useful formulas and tables of parameters associated with the problems.

The Nature of Model Pseudopotentials

Many properties of atoms depend primarily on the valence electrons. The pseudopotential method first suggested by Hellman (3) and by Gombas (4) and given a firm foundation within Hartree-Fock theory by Phillips and Kleinmann (5) is a method for reducing an $N + Z$ electron problem to a problem in Z valence electrons, taking the effect of the core into account by including a "pseudopotential" in a Hamiltonian for the valence electrons. There has been a great deal of recent interest in pseudopotentials because of the desire to do molecular calculations involving atoms with a great many electrons. Both exact pseudopotentials of the Phillips-Kleinmann type and model potentials based on Hartree-Fock results or parameterized using experimental quantities are being exploited in pseudopotential calculations. In this paper attention is focused on model potentials.

The valence electron in a one-valence electron atom using the Atomic Fues Potential of Simons (2) is described by a Schrodinger equation for which the Hamiltonian is given by

$$\hat{H} = -\nabla^2/2 - Z/r + \sum_{l=0}^{\infty} \frac{B_l \hat{P}_l}{r^2} \quad (1)$$

where B_l is an adjustable constant for a given value of the orbital quantum number, l , and \hat{P}_l is a projection operator

which projects out spherical harmonics of a given l . Z is the charge on the core.

The Schrodinger equation for the Simons potential can be solved analytically. The B_l values are fit to one of the states of each l using empirical energies. For example, a single piece of experimental data accounts for all S states. The energy levels of the system obtained from the exact solution are given by

$$E = -2Z^2/[2P + 1 + \{(2l + 1)^2 + 8B_l\}^{1/2}]^2 \quad (2)$$

$$P = 0, 1, 2, \dots$$

The exact wavefunctions of the system are hypergeometric functions (2) and are not discussed here.

The Hellmann-Feynman Theorem

The Hellmann-Feynman theorem states that

$$\frac{\partial E}{\partial \lambda} = \left\langle \psi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \psi \right\rangle \quad (3)$$

(See, for example the discussion in Levine (6)) where λ is a parameter that appears in the Hamiltonian and ψ is a stationary state wavefunction. Since the exact energy level expression for systems with the Hamiltonian given in eqn. (1) is known (eqn. 2), students can be given the problem of calculating expectation values for $1/r$ and $1/r^2$ without actually using the wavefunctions. This can be done by noting that

$$\left\langle \psi \left| \frac{1}{r^2} \right| \psi \right\rangle = \left\langle \psi \left| \frac{\partial \hat{H}}{\partial B_l} \right| \psi \right\rangle \quad (4)$$

and

$$\left\langle \psi \left| \frac{1}{r} \right| \psi \right\rangle = - \left\langle \psi \left| \frac{\partial \hat{H}}{\partial Z} \right| \psi \right\rangle \quad (5)$$

The results of the calculations give

$$\left\langle \psi \left| \frac{1}{r^2} \right| \psi \right\rangle = \frac{16Z^2}{[2P + 1 + \{(2l + 1)^2 + 8B_l\}^{1/2}]^3 \{(2l + 1)^2 + 8B_l\}^{1/2}} \quad (6)$$

and

$$\left\langle \psi \left| \frac{1}{r} \right| \psi \right\rangle = \frac{4Z}{[2P + 1 + \{(2l + 1)^2 + 8B_l\}^{1/2}]^2} \quad (7)$$

By putting in B_l values appropriate to Li, Na, K, Rb, and Cs, the results can be used to examine trends in the behavior of the valence electron in going from one alkali metal to another in various states. Of course, for the alkali metals $Z = 1$. B_l values for alkali metal atoms and singly charged alkaline earth ions are given in Table 1. This problem can also be used to demonstrate that $\langle 1/r^2 \rangle$ is not equal to $\langle 1/r \rangle^2$ and to show trends in "size" in going from Li to Be⁺, for example, where there are the same number of core electrons but different charges on the core ($Z = 1$ and $Z = 2$). The change in orbital size with excitation (P value) can also be examined.

Variation Theorem Problems

The lowest state of a system with a Simons type model potential is an S state. The question can be posed for the alkali metals as to the best approximation to this state of the form

$$\psi = N r^q e^{-cr} \quad (8)$$

where q is an integer and N is a normalizing factor. It can easily be shown that for this system and functions of the form

Table 1. Simons Model Potential Parameters for Alkali Metals^a and Alkaline Earth Ions^b

Atom	B ₀	B ₁	B ₂	B ₃	B ₄
Li	0.467453	-0.060090	-0.00340	0.0016	
Na	0.510188	0.182604	-0.02557	-0.0025	0.000
K	0.682015	0.378552	-0.35484	-0.0239	-0.001
Rb	0.726203	0.474331	-0.55599	-0.04103	-0.010
Cs	0.812414	0.587552	-1.01948	-0.07645	-0.02
Be ⁺	0.63018	-0.06735	-0.00333	0.00112	
Mg ⁺	0.85894	0.43336	-0.07455	-0.00671	
Ca ⁺	1.22213	0.86815	-1.48144	-0.06269	
Sr ⁺	1.35694	1.08377	-1.25970	-0.13286	
Ba ⁺	1.55449	1.32740	-1.29532	-1.04950	

^aHart, G. A., and Goodfriend, P. L., *Molec. Phys.*, **29**, 1109 (1975).

^bSimons, G., *J. Chem. Phys.*, **55**, 756 (1971).

Table 2. Values of f(q)

q	f(q)
0	0.625000
1	0.388021
2	0.258138
3	0.200905

Table 3. Results for Single Function Two Electron Calculations (Hartree Atomic Units) for q = 1

Atom	E _{calc.}	E _{expt.}
Be	-0.862189	-1.0116
Mg	-0.717051	-0.8333
Ca	-0.565828	-0.6607
Sr	-0.524750	-0.6144
Ba	-0.474292	-0.5590

of eqn. (8)

$$\langle \psi | \hat{T} | \psi \rangle = \frac{\epsilon^2}{2(q+1)} \quad (9)$$

$$\left\langle \psi \left| -\frac{1}{r} \right| \psi \right\rangle = -\frac{\epsilon}{q+1} \quad (10)$$

$$\left\langle \psi \left| \sum_{l=0}^{\infty} \frac{B_l \hat{P}_l}{r^2} \right| \psi \right\rangle = \frac{2\epsilon^2 B_0}{(q+1)(2q+1)} \quad (11)$$

The total energy E which is the negative of the ionization energy of the atom, is given by the sum of eqns. (9)–(11). By setting $\partial E/\partial \epsilon = 0$, for any given value of q the optimum value of ϵ is found to be

$$\epsilon = \frac{(2q+1)}{[4B_0 + 2q+1]} \quad (12)$$

Plugging the values of ϵ for $q = 0, 1, 2, 3$, etc. back into the energy equation, one can find the optimum integral value of q . The best energy can then be compared with the ionization potentials of the elements. It should be noted that the exact result will not be obtained, since nonintegral values of q would be required. The exact values of q for the lowest S state are given by

$$q = -\frac{1}{2} + \frac{1}{2} [1 + 8 B_0] \quad (13)$$

Calculations on Two-Valence Electron Atoms

Writing the Hamiltonian for alkaline earth atom valence electrons in the following way

$$H = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} + \sum_{l=0}^{\infty} \frac{B_l \hat{P}_l}{r_1^2} + \sum_{l=0}^{\infty} \frac{B_l \hat{P}_l}{r_2^2} \quad (14)$$

the total valence energy is given by

$$\langle \psi(1,2) | \hat{H} | \psi(1,2) \rangle = E \quad (15)$$

One can seek optimum functions χ , of the form given by eqn. (8) such that

$$\psi(1,2) = \chi(1)\chi(2) \quad (16)$$

The total energy can be written

$$E = \frac{\epsilon^2}{(2q+1)} - \frac{2\epsilon}{(q+1)} + \frac{4B_0\epsilon^2}{(q+1)(2q+1)} + \epsilon f(q) \quad (17)$$

in which the electron repulsion integral is

$$\left\langle \chi(1)\chi(2) \left| \frac{1}{r_{12}} \right| \chi(1)\chi(2) \right\rangle = \epsilon f(q) \quad (18)$$

where

$$f(q) = \frac{1}{q+1} - \frac{1}{2^{q+1}(2q+2)} - \frac{1}{(2q+2)!} \sum_{i=0}^{2q+1} \frac{i}{2^{4q+4-i}} \left(\frac{1}{2q+2} \right) \frac{(4q+3-i)!}{(2q+2-i)!} \quad (19)$$

Either the formula for $f(q)$ or values of $f(q)$ can be given to the student. Values of $f(q)$ for $q = 0, 1, 2$, and 3 are given in Table 2. The optimum value of ϵ is obtained using $\partial E/\partial \epsilon = 0$ yielding

$$\epsilon = \frac{\left[\frac{4}{q+1} - f(q) \right] (2q+1)}{2 \left[1 + \frac{4B_0}{(q+1)} \right]} \quad (20)$$

B_0 values are those of the alkaline earth positive ions (See Table 1). Total energies can be compared with the sum of the first and second ionization energies of the alkaline earths. The best results are obtained with $q = 1$. Results for this case are given in Table 3 along with the experimental energy values. *More elaborate two electron problems can be carried out using the Roothaan formalism (7) by including the pseudopotential in with the bare nuclear Hamiltonian, but they will not be discussed in this paper. More information on these problems can be obtained by contacting the author.*

Hellmann Pseudopotentials and the Virial Theorem

As an example of a problem based upon a model potential other than that of Simons, consider the Hellmann Pseudopotential (3) which yields for a single valence electron the following Hamiltonian

$$\hat{H} = -\nabla^2/2 - Z/r + A \exp(-2Kr)/r \quad (21)$$

One can pose the problem of the appropriate form of the virial theorem for this Hamiltonian. The quantum mechanical virial theorem for a single particle may be written

$$\langle \psi | \hat{T} | \psi \rangle = \frac{1}{2} \langle \psi | r \cdot \nabla V | \psi \rangle \quad (22)$$

where ψ represents a stationary state. The validity of eqn. (22) for

$$V(r) = -Z/r + A \exp(-2Kr)/r \quad (23)$$

follows immediately if the Schrodinger equation with eqn. (21) as Hamiltonian is assumed to be valid. Indeed if the method of Szasz and McGinn (8), is used to fit parameters and STO type wavefunctions to the problem, then the virial theorem can be shown to be automatically satisfied. This illustrates the fact that scaled approximate wavefunctions satisfy the virial theorem as well as exact wavefunctions. Tables of parameters and orbital exponents for wavefunctions for use with this potential can be found in an article by Hart and Goodfriend (9).

Concluding Remarks

No attempt has been made to examine the possibilities for problems in all extant model potentials. Without a doubt, they offer similar types of problems to those described above. Many such potentials are to be found in the literature.

Literature Cited

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