

Variational Perturbation Theory of the Confined Hydrogen Atom

H. E. Montgomery, Jr.

Chemistry Department, Centre College, 600 West Walnut Street, Danville, KY 40422-1394, USA. Tel. (859) 238-5403, e-mail mntgmry@centre.edu

Received: 28 March 2001 Accepted: 15 June 2001/ Published: 16 June 2001

Abstract: Variational perturbation theory was used to solve the Schrödinger equation for a hydrogen atom confined at the center of an impenetrable cavity. Ground state and excited state energies and expectation values calculated from the perturbation wavefunction are comparable in accuracy to results from direct numerical solution.

Keywords: Perturbation theory, confined systems, one-electron atoms

1. Introduction

Confined quantum mechanical systems are a useful model for simulating the effect of external conditions on an enclosed atom. Over sixty years ago, Michels *et al* [1] studied a hydrogen atom confined at the center of an impenetrable cavity and calculated the effects of pressure on kinetic energy and polarizability. This model has subsequently been applied to a wide range of physical problems. The interested reader is referred to Varshni [2] and references therein.

Application of Rayleigh-Schrödinger perturbation theory to confined systems is complicated by the lack of closed form zero-order wavefunctions. However, when a zero-order wavefunction can be obtained, variational perturbation theory provides a method to carry the calculation to high order. In this work we partition the Hamiltonian using a method developed by Sternheimer [3] and calculate energies and expectation values over a range of confinement radii. By comparison with results from direct numerical calculations and with exact results at selected confinement radii, the variational perturbation wavefunctions are shown to be highly accurate. We restricted our attention to the $1s$, $2p$ and $3d$ states which, as the lowest states of a given angular momentum, are readily calculated by variational procedures.

2. Computational Procedures

For a zero-order wavefunction ψ_0 that satisfies the symmetry and boundary conditions of the system of interest, Sternheimer [3] defined the zero-order potential

$$U_0 = \varepsilon_0 - \frac{(T\psi_0)}{\psi_0}, \quad (1)$$

where T is the kinetic energy operator for the system and ε_0 is an arbitrary constant chosen to simplify the potential. The zero-order Hamiltonian H_0 is then given by

$$H_0 = T + U_0. \quad (2)$$

For a Hamiltonian H , the perturbation potential H_1 is

$$H_1 = H - \lambda H_0, \quad (3)$$

where λ is an ordering parameter which will be set equal to 1 at the end of the calculation. Hylleraas-Scherr-Knight variational perturbation theory [4, 5] can be used to calculate corrections to the energy and wavefunction and to evaluate expectation values.

For zero-order wavefunctions, we use

$$\psi(1s) = N_{1s} (r_0 - r) e^{-\alpha r}, \quad (4)$$

$$\psi(2p) = N_{2p} r (r_0 - r) e^{-\alpha r} Y_{10}(\theta, \phi), \quad (5)$$

$$\psi(3d) = N_{3d} r^2 (r_0 - r) e^{-\alpha r} Y_{20}(\theta, \phi), \quad (6)$$

where N is a radial normalization factor, $Y_{lm}(\theta, \phi)$ is a normalized spherical harmonic and α is a variational parameter determined by minimizing $\varepsilon_0 + \varepsilon_1$. The cut-off function $(r_0 - r)$, introduced by de Groot and ten Seldam [6], ensures that $\psi(r_0) = 0$.

The variational perturbation wavefunctions were constructed from trial functions of the form

$$\chi_p = (r_0 - r) e^{-\alpha r} Y_{lm}(\theta, \phi) \sum_n a_n r^n. \quad (7)$$

A typical calculation used fifteen-term trial functions and was carried through ninth-order in the energy. For small values of r_0 the higher powers of r contribute little to the energy and the number of terms in the trial function was reduced. All calculations were performed using quadruple precision arithmetic (~30 decimal digits).

3. Results and Discussion

Table 1 gives the energy corrections for the 1s state over a range of confinement radii. Although the first-order correction is large for small r_0 , the magnitude of the energy corrections for second-order and higher steadily decreases and the energy expansion is in exact agreement with the energies calculated by Goldman and Joslin [7] using direct numerical solution. Similar agreement is observed for the 2p and 3d states.

Table 1. ε_p s in a.u. for the 1s state.

p	$r_0 = 0.1$ a.u.	$r_0 = 1$ a.u.	$r_0 = 10$ a.u.
0	-7.876 050	-0.971 434 42	-0.564 821 13
1	482.777 742	3.362 018 03	0.064 920 13
2	-6.445 089	-0.017 393 87	-0.000 089 37
3	0.583 226	0.000 840 25	-0.000 007 06
4	-0.050 407	-0.000 041 01	-0.000 001 31
5	0.003 841	0.000 001 97	-0.000 000 35
6	-0.000 231	-0.000 000 10	-0.000 000 11
7	0.000 007	0.000 000 01	-0.000 000 04
8	0.000 001		-0.000 000 02
9			-0.000 000 01
Total	468.993 040	2.373 990 86	-0.499 999 27

The radial wavefunction for a free atom has $n - l - 1$ nodes, so the $2s$, $3p$ and $4d$ wavefunctions, where $n = l + 2$, have a single node at

$$r_{node}^{(l+2)} = (l+1)(l+2). \quad (8)$$

When $n = l + 3$, the free atom wavefunction has two nodes, the innermost of which is at

$$r_{node}^{(l+3)} = \frac{1}{2}(l+3)(2l+3 - \sqrt{2l+3}) \quad (9)$$

Similar nodes can be found for $n = l + 4$ and $n = l + 5$.

If r_0 for a confined atom corresponds to a node in the radial wavefunction of the free atom with the same value of l , the confined atom and the free atom have the same energy. Thus, the 1s energy of the confined atom is -0.125 a.u. at $r_0 = 2$ a.u. and -0.05555556 a.u. at $r_0 = 1.90192379$ a.u..

Varshni [8] defined the critical cage radius r_c as the radius of the confining sphere at which the total energy of the atom becomes zero. Sommerfeld and Welker [9] showed that r_c could be obtained from the zeros of $J_p(z)$, the Bessel function of the first kind of order p . If $j_{p,i}$ denotes the i th zero of $J_p(z)$,

$$r_c(n, l) = \frac{1}{8}(j_{2l+1, n-l})^2. \quad (10)$$

For each state, exact energies can be found for three values of r_0 either from simple algebra or from tables of Bessel function zeros.

In order to assess the accuracy of the variational perturbation technique, we calculated the variational perturbation energies at r_c , $r_{node}^{(l+2)}$ and $r_{node}^{(l+3)}$ for the 1s, 2p and 3d states. Rather than tabulate

nearly identical numbers, we note that with the input radius specified to 1×10^{-10} a.u., the exact energy and the ninth-order variational perturbation energy agree to within 1×10^{-10} a.u.

Radial operators such as r and r^2 depend on the wavefunction in regions of configuration space other than those which determine the energy. By comparing expectation values calculated using an approximation method with those calculated by direct solution, we get additional information on the accuracy of the approximate wavefunction. Table 2 gives variational perturbation expectation values for r^{-1} , r and r^2 for the $1s$, $2p$ and $3d$ states over a range of r_0 from 1 to 8 a.u.

Table 2. Variational perturbation expectation values for the confined hydrogen atom.

	r_0 a.u.	$\langle r^{-1} \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$
$1s$	1	2.699 146	0.468 318	0.253 128
	2	1.535 162	0.859 353	0.874 825
	3	1.196 039	1.153 206	1.624 769
	4	1.068 129	1.341 710	2.270 311
	5	1.020 951	1.440 026	2.684 972
	6	1.005 631	1.480 911	2.887 442
	7	1.001 347	1.494 734	2.965 548
	8	1.000 295	1.498 697	2.990 632
$2p$	1	1.894 590	0.581 592	0.363 464
	2	0.972 343	1.141 079	1.405 665
	3	0.667 442	1.675 175	3.045 405
	4	0.517 234	2.180 113	5.188 390
	5	0.429 230	2.651 681	7.726 191
	6	0.372 629	3.085 354	10.536 369
	7	0.334 245	3.476 563	13.484 712
	8	0.307 473	3.821 145	16.430 637
$3d$	1	1.649 154	0.642 711	0.432 834
	2	0.832 952	1.275 252	1.706 763
	3	0.561 312	1.896 775	3.782 271
	4	0.425 847	2.506 340	6.615 972
	5	0.344 883	3.102 913	10.160 199
	6	0.291 199	3.685 353	14.362 564
	7	0.253 131	4.252 409	19.165 526
	8	0.224 849	4.802 716	24.505 985

After a literature survey found few high accuracy expectation values, we decided to calculate a representative set of accurate expectation values. Employing the procedures of Ley-Koo and Rubinstein [10] to solve the Schrödinger equation directly, we used the resulting power series expansions to calculate expectation values. To the accuracy given in Table 2, the expectation values from variational perturbation theory are in exact agreement with the results from direct numerical solution. Thus we conclude that the variational perturbation wavefunctions accurately represent the true wavefunction.

Since the n th-order wavefunction gives the energy through order $2n + 1$ and the expectation values only through order n , expectation value calculations require higher order wavefunctions than do energy calculations. For example, for the $1s(r_0 = 1)$ calculation shown in Table 1, the ψ_p s through $p = 3$ contribute all of the perturbation energies greater than 1×10^{-8} au. For the expectation values of $1s(r_0 = 1)$, it is necessary to calculate the ψ_p s through $p = 6$ to account for all of the expectation value coefficients greater than 1×10^{-6} au.

From the above examples we conclude that variational perturbation theory provides a simple, efficient procedure for calculating properties of the confined hydrogen atom. The techniques of this paper can be readily extended to other confined polynomial potentials or, by imposing the appropriate orthogonality constraints, to additional excited states.

References

1. Michels; A.; de Boer; J.; Bijl, A. Remarks concerning molecular interaction and their influence on the polarisability. *Physica* **1937**, *4*, 981 - 994.
2. Varshni, Y. P. Accurate wavefunctions for the confined hydrogen atom at high pressures. *J. Phys. B: At. Mol. Opt. Phys.* **1997**, *30*, L589 – 1593.
3. Sternheimer, R. M. Electronic polarizabilities of ions from the Hartree-Fock wave functions. *Phys. Rev.* **1954**, *96*, 951 - 968.
4. Hylleraas, E. A. Über den Grundterm der Zweielektronenprobleme von H^+ , He, Li^+ , Be^{++} usw. *Z. Physik* **1930**, *65*, 209 - 225. Translated in Hettner, H. *Quantum Chemistry*, World Scientific: Singapore, 2000, 124 - 139.
5. Scherr, C. W.; Knight, R.E. Two-electron atoms III. A sixth-order perturbation Study of the 1^1S ground state. *Rev. Mod. Phys.* **1963**, *35*, 436 - 442.
6. de Groot, S.R.; ten Seldam, C. A. On the energy levels of a model of the compressed hydrogen atom. *Physica* **1946**, *12*, 669 - 682.
7. Goldman, S.; Joslin, C. Spectroscopic properties of an isotopically compressed hydrogen atom. *J. Phys. Chem.* **1992**, *96*, 6021 - 6027.
8. Varshni, Y. P. Critical cage radii for a confined hydrogen atom. *J. Phys. B: At. Mol. Opt. Phys.* **1998**, *31*, 2849 - 2856.
9. Sommerfeld, A.; Welker, H. Künstliche Grenzbedingungen beim Keplerproblem. *Ann. Phys.* **1938**, *32*, 56 - 65.
10. Ley-Koo, E.; Rubinstein, S. The hydrogen atom within spherical boxes with penetrable walls. *J.*

Chem. Phys. **1979** *71*, 351 - 357.

© 2001 by MDPI (<http://www.mdpi.org>), Basel, Switzerland.