

Variational and perturbative approaches to the confined hydrogen atom with a moving nucleus

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We calculate the ground-state energy and other physical properties of the hydrogen atom inside a spherical box with an impenetrable wall. We apply the variational method and perturbation theory and compare both approximate results. We show that the total, kinetic and potential energies for the moving-nucleus model are greater than those for the case in which the nucleus is clamped at the box center.

I. INTRODUCTION

Atoms and molecules confined into boxes of different shapes and permeability proved to be suitable simple models for the study of the effect of the environment or of high pressure. In the later case the pressure is given by $p = -dE/d\Omega$ where E is the energy and Ω the volume of the confining box. Those models enable us to simulate the effect of pressure on several properties of atoms and molecules, such as, for example, their polarizability[1]. There is a vast literature on the subject and the reader may find suitable reviews elsewhere[2–6].

In all those cases the nucleus was clamped at some chosen point within the box. For example, in the case of an impenetrable spherical box we know that the energy is lowest when the nucleus is clamped at origin and increases as the nucleus approaches the surface[7]. This behavior comes entirely from the interaction between the electron and the wall and does not tell us anything about the effect of the hard surface on the nucleus.

If we have an atom in a real environment we should assume that the nucleus also interacts with that environment. Therefore, it seems reasonable to add that interaction explicitly into the model. The simplest one is that in which both the nucleus and electron are affected exactly in the same way by the impenetrable spherical surface. In such a case we know that the nucleus cannot have zero kinetic energy because of its interaction with the surface and, therefore, the clamped-nucleus approach may not be the most realistic one[8–10].

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It seems more reasonable to assume that a repulsive force on the electron should be an attractive one on the nucleus and conclude that it is more realistic to choose different boundary conditions for each particle at the box surface. However, as a first approximation to more elaborate models it seems sensible to start with an impenetrable wall for both particles and compare the results of this model with the clamped–nucleus approach.

II. THE MODEL

The Hamiltonian operator for a nonrelativistic hydrogen atom is

$$\begin{aligned}\hat{H} &= \hat{T} + \hat{V} \\ \hat{T} &= -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_n}\nabla_n^2 \\ V(r) &= -\frac{e^2}{4\pi\epsilon_0 r}\end{aligned}\tag{1}$$

where m_e and m_n are the masses of the electron and nucleus located at \mathbf{r}_e and \mathbf{r}_n with charges $-e$ and e , respectively, $r = |\mathbf{r}|$, $\mathbf{r} = \mathbf{r}_e - \mathbf{r}_n$, ϵ_0 is the vacuum permittivity and ∇^2 denotes the Laplacian in the coordinates indicated by the subscript.

If the atom is confined to a spherical box of radius R with an impenetrable wall we can formally write the Hamiltonian operator in atomic units as

$$\begin{aligned}\hat{H} &= \hat{T} + V(r) + U(r_e, r_n) \\ \hat{T} &= -\frac{1}{2}\nabla_e^2 - \frac{1}{2m_n}\nabla_n^2, \quad V(r) = -\frac{1}{r} \\ U(r_e, r_n) &= \begin{cases} 0 & \text{if } r_e, r_n \leq R \\ \infty & \text{if } r_e, r_n > R \end{cases}\end{aligned}\tag{2}$$

where $m_n = 1836.15267261$ and the eigenfunctions should vanish when either $r_e = R$ or $r_n = R$.

It is well–known that the virial theorem for such a system is given by[3, 5, 11]

$$R\frac{dE}{dR} = 3\Omega\frac{dE}{d\Omega} = -2\langle\hat{T}\rangle - \langle V\rangle\tag{3}$$

where Ω is the volume of the spherical box. This expression gives us the pressure on the hydrogen atom $p = -dE/d\Omega$ in terms of the kinetic and potential energies. When $R \rightarrow \infty$ we recover the virial theorem for the free hydrogen atom

$$2\langle\hat{T}_r\rangle + \langle V\rangle = 0, \quad \hat{T}_r = -\frac{1}{2m}\nabla^2\tag{4}$$

where \hat{T}_r is the kinetic energy for the relative motion and $m = m_n/(m_n + 1)$ is the reduced mass in atomic units.

III. METHODS OF CALCULATION

A. The variational method

In order to calculate accurate eigenvalues and eigenfunctions of the hydrogen in a box we resort to the generalized Hylleraas basis set that proved useful for three–body Coulomb systems[12–15]. For example, for the S states we

choose a trial function of the form

$$\varphi(r_e, r_n, r) = \left(1 - \frac{r_e}{R}\right) \left(1 - \frac{r_n}{R}\right) \sum_{k=1}^N c_k r_e^{n_k} r_n^{m_k} r^{l_k} e^{-\alpha_k r_e - \beta_k r_n - \gamma_k r} \quad (5)$$

with linear c_k and nonlinear $\alpha_k, \beta_k, \gamma_k$ variational parameters. The explicitly correlated character of these functions ensures accurate energies for the ground and low excited states of free three-body atomic and molecular species with relatively few terms in the expansion. The effect of the Hamiltonian operator (2) on this variational function is simply given by

$$\begin{aligned} \hat{H}\varphi = & -\frac{1}{2} \left(\frac{\partial^2}{\partial r_e^2} + \frac{2}{r_e} \frac{\partial}{\partial r_e} + \frac{r_e^2 - r_n^2 + r^2}{r_e r} \frac{\partial^2}{\partial r_e \partial r} \right) \varphi \\ & - \frac{1}{2m_n} \left(\frac{\partial^2}{\partial r_n^2} + \frac{2}{r_n} \frac{\partial}{\partial r_n} + \frac{r_n^2 - r_e^2 + r^2}{r_n r} \frac{\partial^2}{\partial r_n \partial r} \right) \varphi \\ & - \frac{m_n + 1}{2m_n} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) \varphi - \frac{1}{r} \varphi \end{aligned} \quad (6)$$

A recent pedagogical approach to the confined hydrogen atom with a moving nucleus proposed the simple ansatz

$$\varphi(r_e, r_n) = N(\gamma, R) \left(1 - \frac{r_e}{R}\right) \left(1 - \frac{r_n}{R}\right) e^{-\gamma r} \quad (7)$$

where γ is a variational parameter and $N(\gamma, R)$ the appropriate normalization factor[8, 9]. Since this function yields the correct result when $R \rightarrow \infty$ then it provides accurate ground-state energies for large and moderate values of R . In this paper we propose the straightforward generalization

$$\varphi(r_e, r_n) = \left(1 - \frac{r_e}{R}\right) \left(1 - \frac{r_n}{R}\right) e^{-\alpha r_e - \beta r_n - \gamma r} \sum_{k=1}^N c_k r_e^{n_k} r_n^{m_k} r^{l_k} \quad (8)$$

that may be suitable for the ground and excited S states.

Notice that the cut-off function $(1 - r_e/R)(1 - r_n/R)$ tends to unity as $R \rightarrow \infty$ so that the resulting ansatz (8) will be suitable for the free system. We also expect that under such condition α and β vanish as well as the coefficients c_k of those terms with $n_k \neq 0$ and $m_k \neq 0$.

For comparison we will also consider the hydrogen atom with the nucleus clamped at origin. A suitable trial function is

$$\varphi^{CN}(r) = \left(1 - \frac{r}{R}\right) e^{-\delta r} \sum_{j=0}^N d_j r^j \quad (9)$$

where δ and d_j are nonlinear and linear variational parameters, respectively. This trial function yields the exact S states of the free hydrogen atom when $R \rightarrow \infty$. For brevity we refer to the moving-nucleus case (MNC) and clamped-nucleus case (CNC) from now on.

B. Perturbation theory

In the strong-coupling regime $R \rightarrow 0$ the Coulomb interaction is entirely dominated by the kinetic energy and the problem is almost separable[8–10]. In the first approximation we have two particles moving independently within

the box and we can apply Rayleigh–Schrödinger perturbation theory by splitting the Hamiltonian operator into the zero-order or reference

$$\hat{H}_0 = -\frac{1}{2}\nabla_e^2 - \frac{1}{2m_n}\nabla_n^2 + U(r_e, r_n) \quad (10)$$

and perturbation $\hat{H}' = -1/r$ parts.

The unperturbed eigenfunctions are given by

$$\psi_{nlmn'l'm'}^{(0)}(\mathbf{r}_e, \mathbf{r}_n) = \chi_{nlm}(\mathbf{r}_e)\chi_{n'l'm'}(\mathbf{r}_n) \quad (11)$$

were

$$\chi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta, \phi) \quad (12)$$

and

$$R_{nl}(r) = N_{n,l}j_l(x_{l,n}r/R) \quad (13)$$

In these equations $Y_{lm}(\theta, \phi)$ are the well-known spherical harmonics, $j_l(z)$ is a spherical Bessel function and $x_{l,n}$ its n th zero[16].

IV. RESULTS AND DISCUSSION

Table I shows the total, kinetic and potential energies for the ground state for several values of the box radius R . The first, second, and third rows for each entry shows perturbation and variational results for the MNC and variational results for the CNC, respectively. For simplicity, we restrict our MNC variational calculations to the trial function

$$\varphi(r_e, r_n) = \left(1 - \frac{r_e}{R}\right) \left(1 - \frac{r_n}{R}\right) e^{-\alpha r_e - \beta r_n - \gamma r} (c_1 + c_2 r + c_3 r_n + c_4 r_e) \quad (14)$$

In the CNC we consider Eq. (9) with $N = 4$ that yields as much as five-digits accuracy when compared with the highly accurate results of Aquino et al[17]. On the other hand, the approximate variational MNC energy is expected to be less accurate because the basis set in Eq. (14) is comparatively smaller. However, present results are considerably more accurate than previous ones for this model[8, 9].

First-order perturbation theory is acceptable in the strong-coupling region $R < 1$ au. We appreciate that the perturbation result is systematically greater than the variational one that is known to be a rigorous upper bound. This fact clearly shows that the latter is more accurate even for $R = 0.1$ au where the perturbation result is expected to be fairly accurate. Table I shows that perturbation theory underestimates the nuclear kinetic energy and overestimates the potential energy while, on the other hand, provides a quite reasonable estimate of the electronic kinetic energy.

It is also interesting to compare the variational results for the MNC and CNC. The MNC energy is greater than the CNC one for all values of R . The reason is that the CNC energy is smallest when the nucleus is located at the center of the box that is the particular case chosen here. This effect was discussed earlier by means of a less accurate trial function for the MNC[8, 9]. Table I shows that both the kinetic and potential energies are greater for the MNC.

Table II shows the variational parameters for the trial functions (14) and (9) as well as the expectation values of r_e , r_n and r . Since the magnitude of the nonlinear variational parameter α is negligible for all values of R we have

set it equal to zero. On the other hand, β is quite large for small R and decreases as R increases. The remaining nonlinear parameter γ decreases with R reaches a minimum and then increases asymptotically towards the free-atom value. Those exponential parameters suggest that the nucleus is localized about the box center whereas the electron is localized about the nucleus (though not so strongly because $\beta > \gamma$ for all R). The fact that $\langle r_n \rangle < \langle r_e \rangle \approx R/2$ supports this conjecture. Table II also shows that $\langle r \rangle_{MNC} \approx \langle r \rangle_{CNC}$.

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TABLE I: Total, kinetic and potential energies for the confined hydrogen atom for several values of the box radius. The entries stand for MNC perturbation theory, MNC variational method and CNC variational method, respectively

R	E	$\langle T \rangle$	$\langle T_e \rangle$	$\langle T_n \rangle$	$\langle V \rangle$
0.1	475.88825	493.74898	493.48022	0.26876	-17.86073
	473.84272	497.55784	495.52046	2.03739	-23.71513
	468.99313	493.59225	-	-	-24.59911
0.2	114.50688	123.43724	123.37006	0.06719	-8.93037
	112.47785	124.54287	123.91907	0.62381	-12.06502
	111.07107	123.48629	-	-	-12.41522
0.3	48.90742	54.86100	54.83114	0.02986	-5.95358
	47.28928	55.44914	55.13094	0.31820	-8.15987
	46.59279	54.94902	-	-	-8.35623
0.4	26.39413	30.85931	30.84251	0.01680	-4.46518
	25.06003	31.26099	31.06244	0.19855	-6.20096
	24.63398	30.96278	-	-	-6.32881
0.5	16.17781	19.74996	19.73921	0.01075	-3.57215
	15.03997	20.06358	19.92556	0.13802	-5.02361
	14.74805	19.86217	-	-	-5.11412
0.6	10.73846	13.71525	13.70778	0.00747	-2.97679
	9.74237	13.98064	13.87803	0.10261	-4.23827
	9.52774	13.83361	-	-	-4.30586
0.7	7.52498	10.07651	10.07102	0.00548	-2.55153
	6.63550	10.31303	10.23317	0.07986	-3.67754
	6.46994	10.19984	-	-	-3.72990
0.8	5.48224	7.71483	7.71063	0.00420	-2.23259
	4.67560	7.93312	7.86889	0.06424	-3.25753
	4.54339	7.84251	-	-	-3.29912
0.9	4.11114	6.09567	6.09235	0.00332	-1.98453
	3.37058	6.30211	6.24913	0.5298	-2.93153
	3.26219	6.22741	-	-	-2.96522
1.0	3.15142	4.93749	4.93480	0.00269	-1.78607
	2.46468	5.13617	5.09161	0.04456	-2.67149
	2.37399	5.07314	-	-	-2.69915
1.1	-	-	-	-	-
	1.81475	4.27426	4.23620	0.03807	-2.45952
	1.73761	4.22006	-	-	-2.48245
1.2	-	-	-	-	-
	1.33794	3.64094	3.61044	0.03049	-2.30300
	1.26931	3.57213	-	-	-2.30282
1.3	-	-	-	-	-
	0.97551	3.12685	3.10009	0.02676	-2.15133
	0.91704	3.06876	-	-	-2.15172
1.4	-	-	-	-	-
	0.69758	2.71961	2.69594	0.02367	-2.02203
	0.64711	2.67018	-	-	-2.02307
1.5	-	-	-	-	-

R	E	$\langle T \rangle$	$\langle T_e \rangle$	$\langle T_n \rangle$	$\langle V \rangle$
2.0	–	–	–	–	–
	–0.09946	1.43084	1.41801	0.01283	–1.53031
	–0.12500	1.41016	–	–	–1.53515
3.0	–	–	–	–	–
	–0.41078	0.78067	0.77452	0.00615	–1.19145
	–0.42397	0.77206	–	–	–1.19603
4.0	–	–	–	–	–
	–0.47520	0.59178	0.58854	0.00325	–1.06699
	–0.48327	0.58486	–	–	–1.06813
5.0	–	–	–	–	–
	–0.49138	0.53155	0.52961	0.00194	–1.02293
	–0.49642	0.52453	–	–	–1.02095
6.0	–	–	–	–	–
	–0.49615	0.51194	0.51064	0.00130	–1.00809
	–0.49928	0.50635	–	–	–1.00563
7.0	–	–	–	–	–
	–0.49784	0.50515	0.50420	0.00096	–1.00299
	–0.49986	0.50148	0.50148	–	–1.00135
8.0	–	–	–	–	–
	–0.49857	0.50256	0.50180	0.00075	–1.00113
	–0.49997	0.50032	0.50032	–	–1.00029
9.0	–	–	–	–	–
	–0.49894	0.50145	0.50082	0.00062	–1.00039
	–0.50000	0.50006	0.50006	–	–1.00006
10.0	–	–	–	–	–
	–0.49916	0.50070	0.50013	0.00057	–0.99985
	–0.50000	0.50002	0.50002	–	–1.00002

TABLE II: Variational parameters for the trial functions (14) and (9) ($N = 4$) and some expectation values

R	β	γ	c_1	c_2	c_3	c_4		$\langle r_e \rangle$	$\langle r_n \rangle$	$\langle r \rangle_{MNC}$
		δ	d_0	d_1	d_2	d_3	d_4			$\langle r \rangle_{CNC}$
0.1	71.386	12.285	0.056	1.000	-0.210	0.446		0.050	0.017	0.052
	-	4.915	0.001	0.014	0.004	-1.154	2.836	-	-	0.050
0.2	40.494	6.305	0.120	1.000	-0.203	0.514		0.099	0.031	0.102
	-	1.068	0.095	0.531	-2.000	-1.603	-0.639	-	-	0.099
0.3	29.340	4.287	0.195	1.000	-0.203	0.588		0.148	0.044	0.152
	-	1.321	0.140	0.551	-0.946	-1.275	-0.567	-	-	0.147
0.4	23.400	3.267	0.286	1.000	-0.207	0.670		0.196	0.055	0.200
	-	1.267	0.261	0.767	-0.768	-1.127	-0.513	-	-	0.195
0.5	19.647	2.651	0.397	1.000	-0.214	0.767		0.243	0.066	0.248
	-	1.217	0.419	0.977	-0.593	-0.974	-0.437	-	-	0.242
0.6	17.031	2.237	0.535	1.000	-0.225	0.883		0.290	0.077	0.295
	-	1.156	0.617	1.171	-0.446	-0.848	-0.333	-	-	0.289
0.7	15.088	1.939	0.694	0.974	-0.233	1.000		0.337	0.087	0.341
	-	1.095	0.797	1.253	-0.293	-0.706	-0.216	-	-	0.335
0.8	13.578	1.713	0.781	0.825	-0.215	1.000		0.382	0.097	0.387
	-	1.041	0.958	1.262	-0.163	-0.586	-0.126	-	-	0.380
0.9	12.365	1.536	0.867	0.685	-0.197	1.000		0.427	0.107	0.431
	-	1.001	1.091	1.225	-0.052	-0.485	-0.065	-	-	0.425
1.0	11.365	1.393	0.954	0.551	-0.182	1.000		0.471	0.117	0.475
	-	1.011	0.972	0.980	0.073	-0.330	-0.033	-	-	0.468
1.1	17.414	0.480	0.025	-0.091	1.000	0.095		0.515	0.123	0.518
	-	1.212	0.885	1.000	0.233	-0.074	-0.124	-	-	0.511
1.2	16.215	0.481	0.028	-0.095	1.000	0.099		0.557	0.132	0.560
	-	1.216	0.948	1.000	0.272	-0.022	-0.099	-	-	0.553
1.3	15.168	0.482	0.031	-0.100	1.000	0.103		0.599	0.141	0.602
	-	1.224	0.993	0.989	0.298	0.019	-0.076	-	-	0.595
1.4	14.243	0.485	0.033	-0.104	1.000	0.107		0.640	0.150	0.642
	-	1.264	1.000	0.983	0.328	0.071	-0.061	-	-	0.635
1.5	13.418	0.488	0.037	-0.109	1.000	0.112		0.681	0.159	0.681
	-	1.279	1.000	0.951	0.335	0.093	-0.041	-	-	0.675

R	β	γ	c_1	c_2	c_3	c_4				
		δ	d_0	d_1	d_2	d_3	d_4	$\langle r_e \rangle$	$\langle r_n \rangle$	$\langle r \rangle_{MNC}$ $\langle r \rangle_{CNC}$
2.0	10.303	0.510	0.056	-0.131	1.000	0.133		0.869	0.204	0.864
	-	1.348	1.000	0.841	0.385	0.062	0.045	-	-	0.859
3.0	4.498	0.565	1.000	-0.459	0.312	0.452		1.178	0.319	1.147
	-	0.922	1.000	0.243	0.091	-0.012	0.012	-	-	1.153
4.0	2.974	0.642	1.000	-0.324	-0.015	0.319		1.391	0.449	1.320
	-	0.400	1.000	-0.350	0.086	-0.012	0.001	-	-	1.342
5.0	2.159	0.711	1.000	-0.254	-0.063	0.251		1.539	0.599	1.408
	-	0.424	1.000	-0.375	0.087	-0.012	0.001	-	-	1.440
6.0	1.643	0.768	1.000	-0.200	-0.090	0.201		1.657	0.761	1.450
	-	0.465	1.000	-0.367	0.079	-0.010	0.001	-	-	1.481
7.0	1.296	0.813i	1.000	-0.157	-0.109	0.165		1.770	0.930	1.470
	-	0.510	1.000	-0.346	0.068	-0.008	0.000	-	-	1.495
8.0	1.043	0.851	1.000	-0.122	-0.126	0.139		1.887	1.106	1.480
	-	0.555	1.000	-0.319	0.057	-0.006	0.000	-	-	1.499
9.0	0.841	0.886	1.000	-0.089	-0.142	0.118		2.018	1.295	1.486
	-	0.601	1.000	-0.287	0.046	-0.004	0.000	-	-	1.500
10.0	0.747	0.910	1.000	-0.067	-0.151	0.102		2.104	1.412	1.490
	-	0.935	1.000	0.032	0.009	-0.001	0.000	-	-	1.500