

Electronic trajectories in atomic physics: the chemical bond in the H_2^+ ion

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July 6, 2020

Abstract

The H_2^+ ion is the simplest example in which a chemical bond exists, created by one electron between two protons. As all chemical bonds, it is usually considered inexplicable in a classical frame. Here, in view of the extremely large velocities attained by the electron near the protons, we consider a relativistic extension of the standard classical three-body model. This has a great impact, since the reference unperturbed system (clamped protons) is no more integrable, and indeed by molecular dynamics simulations we find that the modification entails the existence of a large region of strongly chaotic motions for the unperturbed system, which lead, for the full system, to a collapse of the molecule. For motions of generic type, with the electron bouncing between the protons, there exists an open region of motions regular enough for producing a bond. Such a region is characterized by the property that the electron's trajectories have an angular momentum p_φ along the inter nuclear axis of the order of the reduced Planck's constant \hbar . Moreover, special initial data exist for which the experimental bond length and oscillation frequency of the protons (but not the dissociation energy) are well reproduced. Also well reproduced is

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the quantum potential, albeit only in an extended interval about the minimum.

1 Introduction

Many problems of atomic or molecular physics are dealt with through models in which one has a certain number of positively charged ions (considered as point particles) and of electrons, with mutual Coulomb forces. It is well known that the dynamics of the ions can be investigated in a sufficiently accurate way by describing the system through a classical model (namely, one involving Newton equations) in which the electrons don't show up, their effect being substituted by suitable effective potentials acting among the ions.

An analogous procedure is used in the case of ionic crystals, in which one introduces effective potentials acting among the ions, now in order to take into account the dynamical role of the internal shells of electrons. It is thus possible to perform accurate numerical simulations and compute significant quantities, such as time-correlation functions and more in general response functions, as is usually done in the research field of molecular dynamics. In such a way it was possible to compute, in terms of classical ionic trajectories, physical macroscopic quantities such as infrared absorption spectra (see Refs. [13] and [7]) and dispersion relations (see Ref. [19]). In particular, it was possible to exhibit the existence of polaritons (see Ref. [19]), a bifurcation phenomenon concerning the dispersion relations and due to retardation, a proof of which in a microscopic quantum model is still lacking. This is due to the difficulties met by quantum electrodynamics in dealing with retardation of the electric forces in microscopic models of matter in bulk. Such a difficulty does not occur in a classical frame, due to the Wheeler-Feynman identity, which was conjectured by those authors in the year 1945, and was eventually proven, first in a particular model (see [5]) and then in general (see [6]). For the aims of the present paper the relevant consequence of such an identity is that it produces a cancellation of the radiation reaction forces, and thus eliminates the radiation losses for matter in bulk, which constituted the severest obstacle to the use of classical models in atomic physics.

Concerning the effective potentials, if historically, starting from Born they were introduced in a phenomenological way through analytical expressions containing several parameters, in recent times, with the advent of more and more powerful computers, the tendency is to obtain them making use of

the quantum dynamics of the electrons in a suitable approximate form, for example through the Carr–Parrinello method [8] or through path integral molecular dynamics (see for example Ref. [10]). Now, from the computational point of view quantum dynamics is much more demanding than the classical one. One thus sees how important is the problem of understanding whether the effective potentials due to the motion of the electrons, dealt with in a classical frame, may give correct results or not. Said in a more explicit way, the question is whether initial data for the electrons exist such that, by (numerically) solving the newton equations for the complete system (ions plus electrons), the motion of the ions turns out to be consistent with the experimental data.

However, when dealing with a generic system involving more than one electron, dynamical instabilities are met, by which all the electrons but one escape far away from the ions, so that atoms and molecules cannot be formed. Moreover, this occurs also in the zero-th order approximation of perturbation theory, in which the ions are clamped. Instead this the difficulty doesn't show up for systems with just one electron.

Now, the simplest case in which the interplay among ions and electrons occurs in nature, is that of the H_2^+ ion of the hydrogen molecule H_2 , which involves two protons and just one electron, the latter producing a chemical bond among the ions. Such a case is thus amenable to a classical investigation. This is an interesting opportunity, if one aims at clarifying the relations between quantum and classical mechanics. Indeed, on the one hand, in the words of Gutzwiller (Ref. [14], page 36) the H_2^+ problem “*can be rated, with only slight exaggeration, as the most important in quantum mechanics*”. On the other hand, the chemical bond in H_2^+ is sometimes “explained” in quantum terms using the superposition principle, so that it might appear to be altogether inconceivable in a classical frame.[24]

Now, by solving the newton equations for the three particles we showed that, for suitable initial data, the motion of the ions can be described as a two-body system (the protons) with a central effective potential $V_{\text{eff}}(r)$, in which the motion of the electron doesn't explicitly show up. In fact, there exist initial data such that the potential presents a well, so that the molecule is formed, and the distance among the ions oscillates around a well definite mean value. So, both the “bond length” and the protons' vibrational frequency have well definite values, which depend on the energy (temperature) of the ions. Obviously, the effective potential depends on the electronic state chosen (i.e., on the electron's initial data). In fact, it has also been possible

to determine the existence of at least one initial state (in a certain sense an exceptional one, leading to a trajectory in the equatorial plane, as will be better discussed later) that accounts for the experimental bond length and frequency of the infrared oscillations. The effective potential corresponding to such a case is reported in Figure 1, together with that predicted¹ by the quantum Born-Oppenheimer approximation [4]; in the enlargement exhibited in the right panel the harmonic approximation too is reported. As one sees, the classical and the quantum potentials agree in a surprisingly good way in an extended interval about the minimum, up to not too large vibrations (say, for vibrational levels with $n < 5$, which corresponds to $\Delta E = 0.05$ hartree), whereas they are very different for $r \rightarrow +\infty$. The latter fact implies in particular that the dissociation energy is not well reproduced. On the other hand, no systematic research was performed for the initial data that may best reproduce the whole phenomenology, which actually was not the scope of our work.

The model we consider is a semi-relativistic extension of the standard Coulomb three-body problem, inasmuch as the energy of the electron was taken in its relativistic form. While such a modification (which is necessary, due to the very high velocities the electron attains near the protons²) might appear to be just a minor one, it will be seen to have a relevant impact for the existence of the effective potential. The reason is understood if one looks at the existence of the potential in the spirit of perturbation theory, in which the perturbation parameter is the ratio m/M of electron to proton mass, so that the zero-th approximation corresponds to clamped protons, as in the work of Born and Heisenberg [3] which was performed in a classical frame in the year 1924.³ Indeed, in the non relativistic case the unperturbed approximation is integrable, in the familiar sense of admitting action-angle variables (a fact known since the time of Euler), so that perturbation theory in principle can be applied in its standard form. Instead, in the relativistic case the system

¹The quantum potential was calculated according to Ref. [17], by analytical solution of the Schroedinger equation for the electron in the Born–Oppenheimer approximation. The numerical results were found to agree with available data in the literature (see [26], [25]).

²In the chaotic region - see below - one finds velocities v with $v/c \simeq 0.8$.

³Unfortunately, we were not yet able to fully understand the content of the work of Born and Heisenberg who, already in the second page of their paper, explicitly indicate as their aim, to explain, by means of classical perturbation theory, “*the motion of a molecule, as a mechanical system of nuclei and electrons*”. We hope to be able to come back to this point in the future.

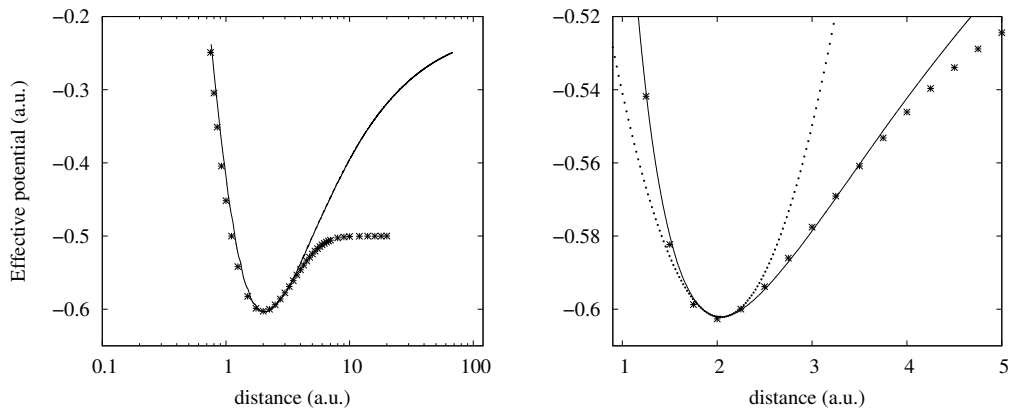


Figure 1: Effective potential as a function of proton distance, computed for suitably chosen initial data (continuous line), together with the quantum potential in the Born-Oppenheimer approximation (stars). Distance and potential are given in atomic units (a.u.). Left: comparison in the whole explored distance range, with logarithmic scale on the horizontal axis. Right: detail of the minimum region, and comparison with the harmonic approximation (dotted line). One can appreciate that the agreement with the quantum potential holds up to rather large nonlinearities, actually up to an energy of -0.55 hartree.

is no more integrable and in fact, as will be shown later, extended regions of strong chaoticity show up already in the unperturbed case. Thus one has a coexistence of regular and chaotic regions, and a binding effect can exist only in the regular (or nearly integrable) ones. For generic motions (in which the electron bounces between the two protons) near-integrability was found to hold only if the angular momentum p_φ of the electron along the inter-nuclear axis is above thresholds of the order of the reduced Planck constant \hbar , and this, in a model that contains, as atomic parameters, only the electronic and protonic masses, the electronic charge e and the speed of light c . This implies that, for motions of generic type, in the semi-relativistic model the effective potential can exist only for initial data which are dynamically constrained to lie within a realistic domain, so that a consistent fit of the experimental data is possible, and this is perhaps the most physical relevant result of the present paper. Whether this fact be a simple coincidence or may have a deeper significance, we are unable to say at the moment.

The studies dealing with the possibility of describing the chemical bond of the H_2^+ ion in terms of its newtonian trajectories have a long history, with a first phase (see [2], [23], [22], [11], [18], [28]) initiated by the Bohr paper of the year 1913 and centered about the sixty-pages long paper of Pauli of the year 1922, and a more recent phase (see [27], [26], [21], [16]). Such works were performed in the spirit of the “old quantum theory”, in which classical trajectories are considered, and quantization enters only in the choice of the initial data in phase space. A different approach, more similar to ours, is taken in the paper [12] of Fuchigami and Someda. Such authors study the full non relativistic three-body problem by classical mechanics, with the aim of investigating the evolution of the adiabatic invariants near resonant regions, whereas the problem of the effective potential is not investigated. Furthermore, such a study is confined to motions taking place in a plane through the inter-nuclear axis.

The present paper is organized as follows. In Section 2 we first illustrate the three-body model used in our study. In the same Section we also discuss how the theory of adiabatic invariants can explain that the dynamics of the electron may decouple from that of the ions, producing a binding effect describable, in a first approximation, by an effective potential. We finally point out what relevance the presence of chaotic motions has for of the stability of the H_2^+ ion. In Section 3 we first illustrate the method we devised for determining the effective potential from the trajectories of the full system, and also illustrate the results obtained. The conclusions then follow.

2 The model and the averaging principle

We now illustrate how, in the familiar spirit of perturbation theory (essentially, the principle of the mean) the possibility itself exists of describing classically the motion of the protons as decoupled from that of the electron, the only effect of the latter being of producing an “effective” binding force among the protons. The reason is that, in virtue of the great mass difference between electron and protons, in the full system there exist “fast” degrees of freedom related to the motion of the electron, and “slow” ones related to the protons. On the other hand, in perturbation theory the averaging principle states that the system obtained by averaging over the fast variables describes well (up to a certain time scale) the motion of the slow ones, on which the system still depends. In the standard model of the ion H_2^+ , i.e. a single non relativistic electron of mass m interacting with two (point-like) protons having a much larger mass M , all with a charge of the same modulus e , the hamiltonian is

$$H = \frac{p^2}{2m} - \frac{e^2}{|\mathbf{r} - \mathbf{x}_1|} - \frac{e^2}{|\mathbf{r} - \mathbf{x}_2|} + \frac{P_1^2}{2M} + \frac{P_2^2}{2M} + \frac{e^2}{|\mathbf{x}_1 - \mathbf{x}_2|}, \quad (1)$$

where \mathbf{p} and \mathbf{r} are the coordinates (momentum and position) of the electron, while \mathbf{P}_i and \mathbf{x}_i are the coordinates of the two protons. It is well known that for the electronic hamiltonian

$$H_e = \frac{p^2}{2m} - \frac{e^2}{|\mathbf{r} - \mathbf{x}_1|} - \frac{e^2}{|\mathbf{r} - \mathbf{x}_2|} \quad (2)$$

with \mathbf{x}_1 and \mathbf{x}_2 fixed (the Euler two fixed-centers problem), there exists a canonical transformation leading to action-angle variables $\mathbf{J}, \boldsymbol{\varphi}$ such that it takes the form

$$H_e = H_e(\mathbf{J}, R), \quad (3)$$

which depends only on the actions, in addition to a parametric dependence on the distance

$$R = |\mathbf{x}_1 - \mathbf{x}_2| \quad (4)$$

among the protons, i.e. the system is integrable. Indeed, in addition to energy and angular momentum along the inter-nuclear axis, a further integral Ω exists, which is the analogue of the Laplace-Runge-Lenz integral occurring

in the case of spherical symmetry. Such an integral turns out to have the form (see formula (2.6) of Ref. [26])

$$\Omega = \mathbf{L}_1 \cdot \mathbf{L}_2 + mRe^2 (\cos \theta_1 - \cos \theta_2) ,$$

where \mathbf{L}_i are the angular momenta of the electron with respect to the two protons, and θ_i are the angles between the position vectors of the electron with respect to the protons, and the inter nuclear axis.

Furthermore, the angles $\boldsymbol{\varphi}$ turn out to be in general fast variables, i.e. their frequencies $\boldsymbol{\omega} = \partial H_e / \partial \mathbf{J}$ are in general much larger than the speeds of the other electronic variables. If now one applies such a transformation to the full hamiltonian (1), in the new variables the hamiltonian takes the form

$$H = H_e(\mathbf{J}, R) + \frac{P_1^2}{2M} + \frac{P_2^2}{2M} + \frac{e^2}{R} + F(\mathbf{J}, \boldsymbol{\varphi}, \mathbf{P}_1, \mathbf{P}_2, R) , \quad (5)$$

with a certain function F , so that the full hamiltonian appears as a “small” perturbation of the hamiltonian

$$H_0 = \frac{P_1^2}{2M} + \frac{P_2^2}{2M} + \frac{e^2}{R} + H_e(\mathbf{J}, R) \quad (6)$$

(we recall that the perturbing function F comes in because R enters parametrically in H_e , and thus also in the generating function S of the canonical transformation, so that the modulus $|\mathbf{P}_1 - \mathbf{P}_2|$ transforms into $|\mathbf{P}_1 - \mathbf{P}_2| + \partial S / \partial R$).

Now, perturbation theory shows (for a modern development see for example Ref. [1]) that, if the frequencies $\boldsymbol{\omega}$ are sufficiently large, then the motion of the system should be “well” described by the full hamiltonian averaged over the angles, i.e. essentially by the hamiltonian H_0 (6). On the other hand, such a hamiltonian exhibits in a manifest way the main fact of interest here, namely, that the electronic energy $H_e(\mathbf{J}, R)$ plays the role of an effective potential among the protons, analogously to what occurs in the quantum case. A further study would then establish whether such an effective potential may overcome the repulsion between the protons, thus ensuring the existence of a stable state of the ion H_2^+ . Actually, one should rather speak of a “possibly meta stable” state, because the theorem of the mean ensures that the result (i.e. the constancy of the actions \mathbf{J}) holds only over a certain time scale, which is long, but not infinitely long. The existence of really stable states would require a KAM approach (which we disregard here, as we also

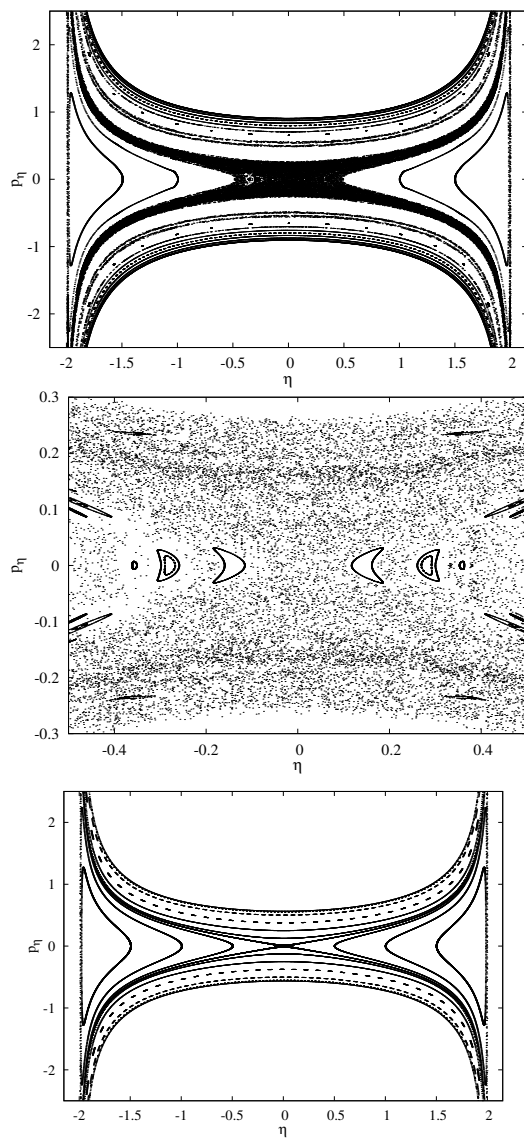


Figure 2: Poincaré section $p_\xi = 0$ (see text), for the relativistic two fixed-centers model, for energy $E = -0.606$ and angular momentum $l = 0.1$ (in atomic units), upper and middle panel. For the sake of comparison, the non relativistic integrable model is exhibited in the lower panel. Notice that $\eta = 0$ corresponds to the equatorial plane. The upper panel shows a large chaotic zone, in a region where an orbit should lie in order to be binding. In the middle panel an enlargement of the chaotic zone is shown, exhibiting some of the structures which are present.

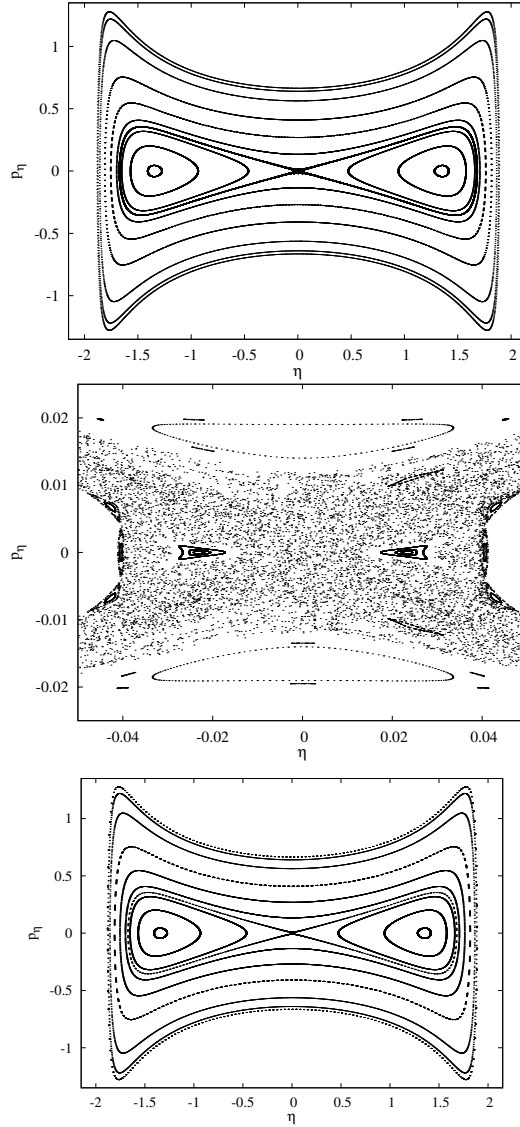


Figure 3: Same as Figure 2, still for energy $E = -0.606$ but now for a higher value $l = 0.6$ of the angular momentum. The upper panel shows that now the central chaotic zone did shrink, while the vast majority of the orbits appear to lie on smooth curves. In the central panel an enlargement (ten times greater than in figure 2) of the chaotic zone is shown. The lower panel refers to the non relativistic model.

do for a study of the non resonant set, which would be required for a rigorous application of the theorem of the mean).

However, physically the standard model defined by hamiltonian (1) is not completely coherent because, for initial data in the atomic domain, the velocities of the electron may become a relevant fraction of the speed of light c . So we chose to use the partially relativistic model with hamiltonian

$$H = mc^2 \sqrt{1 + \frac{p^2}{m^2 c^2}} - \frac{e^2}{|\mathbf{r} - \mathbf{x}_1|} - \frac{e^2}{|\mathbf{r} - \mathbf{x}_2|} + \frac{P_1^2}{2M} + \frac{P_2^2}{2M} + \frac{e^2}{|\mathbf{x}_1 - \mathbf{x}_2|} . \quad (7)$$

But then the electronic energy (with $\mathbf{x}_1, \mathbf{x}_2$ fixed)

$$H_e = mc^2 \sqrt{1 + \frac{p^2}{m^2 c^2}} - \frac{e^2}{|\mathbf{r} - \mathbf{x}_1|} - \frac{e^2}{|\mathbf{r} - \mathbf{x}_2|} , \quad (8)$$

is no more completely integrable, since it presents only two (rather than three) integrals of motion, i.e. the energy and the component p_φ of the angular momentum along the inter-nuclear axis, while the analogue of the Laplace-Runge-Lenz integral is lost.

The non integrability of the *clamped* semi-relativistic hamiltonian (8) is very clearly exhibited through the familiar tool of the “surfaces of section”, which we now recall. Exploiting the constancy of the angular momentum p_φ , one can pass to the corresponding reduced hamiltonian, and, using cylindrical coordinates with the z axis along the protons, the electronic hamiltonian (8) takes the form

$$H_e = mc^2 \sqrt{1 + \frac{1}{m^2 c^2} \left(p_z^2 + p_\rho^2 + \frac{l^2}{\rho^2} \right)} - \frac{e^2}{\sqrt{\rho^2 + (z - z_1)^2}} - \frac{e^2}{\sqrt{\rho^2 + (z - z_2)^2}} . \quad (9)$$

where $\rho = \sqrt{x^2 + y^2}$ is the distance of the electron from the inter-nuclear axis and l is a given value of the angular momentum p_φ of the electron along that axis. So one is now dealing with a system with two degrees of freedom in a phase space \mathbb{R}^4 and thus, as in the familiar Hénon-Heiles case [15], by fixing the value of energy one is reduced to a three-dimensional subset

(the “energy surface”). The mapping on a Poincaré surface of section is finally constructed by computing orbits and intersecting them by a given two-dimensional surface.

In figures 2 and 3 such a surface is the plane $p_\xi = 0$, where ξ and η are the familiar elliptic coordinates defined (using Arnold’s conventions) by $\xi = |\mathbf{r} - \mathbf{x}_1| + |\mathbf{r} - \mathbf{x}_2|$ and $\eta = |\mathbf{r} - \mathbf{x}_1| - |\mathbf{r} - \mathbf{x}_2|$, while p_ξ, p_η are the corresponding conjugate momenta. In Fig 2, the values of η and p_η are reported for $E = -0.606$ and $l = 0.1$ (l denoting the value of p_φ), while the distance between the protons is taken equal to 2 (in atomic units). The whole section is shown in the upper panel, where one sees that the points corresponding to the different orbits, instead of being all located on regular curves, as would occur if a third integral did exist, occupy fuzzy regions, particularly in the central part. This feature is emphasized in the enlargement of the central part, which is reported in the middle panel. A single orbit is seen to invade a two-dimensional region, and other structures are exhibited, that one may be tempted to qualify as fractals. In such a case it is no more possible to introduce action-angle variables which would make the electronic hamiltonian depend on the actions only, as occurs in the (integrable) non-relativistic case which is illustrated, for the sake of comparison, in the lower panel. Instead, if for the angular momentum p_φ one fixes a larger value such as $l = 0.6$, the surface of section, shown in Fig. 3, appears to be much more regular, suggesting that in such a case a “quasi integral of motion” exists, the different values of which do identify each of the invariant curves exhibited. Such a further integral, by the way, constitutes in atomic physics the analog of the celebrated “third integral” of celestial mechanics, to which the whole scientific life of G. Contopoulos was devoted (a very recent review is given in Ref. [9]). In the presence of such a third integral, a transformation can be found that eliminates the angles from the electronic hamiltonian (possibly up to a very small remainder) in a very extended open set in phase space. In such a situation one might presume that the full semi-relativistic hamiltonian (7) averaged over the angles provides a good approximation for the motion of the slow variables, i.e., for the motion of the protons. As previously explained, in such a situation the electronic energy plays the role of a potential which complements the repulsive Coulomb potential between the protons.

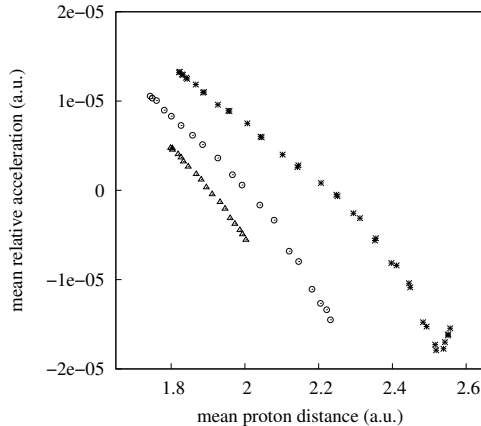


Figure 4: Radial component of the mean relative acceleration of protons vs. their mean distance, for three different trajectories. The points are seen to lie on different curves, depending on the initial data.

3 The full three-body system

In the previous section it was explained how, in the spirit of perturbation theory, it is possible at all to conceive that, analogously to what occurs in quantum mechanics, in classical mechanics too the motion of the protons can be described by eliminating the motion of the electron and replacing it by a suitable contribution to an effective potential acting between the protons. More precisely, this is expected to occur only in a suitable domain of phase space, where the dynamics of the system is regular rather than chaotic, i.e. a “third integral” exists. However, the actual implementation of such a program for the full semi-relativistic hamiltonian (7) considered in this paper, requires the establishment of delicate results within perturbation theory which, in view of their complexity, we refrain from explicitly facing here. By the way, for the aims indicated in the introduction, such an investigation would not even be fruitful.

So we resolved to limit ourselves, in the present work, to just check numerically that a bond exists for suitable initial data of the electron. Actually the check required to devise a suitable procedure in order to determine the effective potential, making reference only to the trajectories, i.e., concretely, to the numerically computed ones. As shown in the previous section, the

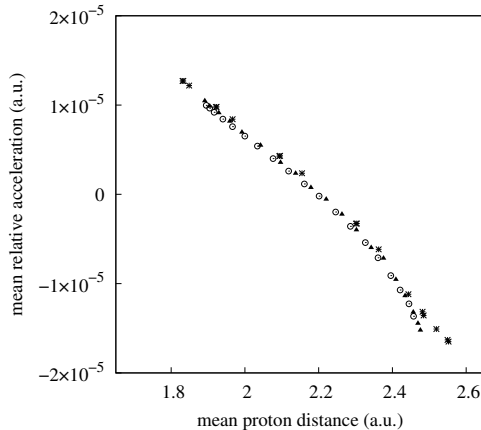


Figure 5: Same as Fig. 4 for three different initial data with the same electronic state. The curves now superpose.

effective potential would emerge if one were able to pass from the actual motion of the electron to a motion averaged over the associated fast angles. As such angles are not well defined in the relativistic case (which we have shown to be non integrable in the Liouville sense) we decided to replace such an averaging procedure by time averages. The very simple idea is to consider the relative distance vector $\mathbf{x}_1(t) - \mathbf{x}_2(t)$ of the protons, and its time average, that we denote simply by $\mathbf{R}(t)$, over a suitable time interval Δt . Then one checks whether the radial part a_R of $\ddot{\mathbf{R}}$ is a function of R , and in such a case a radial force turns out to be defined.

The numerical implementation is then obvious. The equations of motion were numerically integrated with a regularized symplectic algorithm that will be described later (a regularization is indeed necessary, since nothing forbids the electron from coming arbitrarily close to the protons during its motion). Trajectories $\mathbf{r}(t_j)$, $\mathbf{x}_1(t_j)$, $\mathbf{x}_2(t_j)$ were thus obtained for the electron and the two protons. Then, having fixed a suitable time-interval Δt (actually, $\Delta t \simeq 6.4 \cdot 10^{-16}$ seconds⁴ in our computations), time averages were taken of the relative distance vector, namely,

$$\mathbf{R}(t_j) \stackrel{\text{def}}{=} \frac{1}{2N} \sum_{k=j-N+1}^{j+N} (\mathbf{x}_1(t_k) - \mathbf{x}_2(t_k)) , \quad (10)$$

⁴This corresponds to about a million of typical integration steps.

where N is determined by the condition $t_{j+N} - t_{j-N+1} = \Delta t$, whereas the values of j were chosen as multiples of $2N$. The relative acceleration $\ddot{\mathbf{R}}$ at time t_j was then computed through the usual approximation

$$\ddot{\mathbf{R}}(t_j) \stackrel{\text{def}}{=} \frac{\mathbf{R}(t_{j+1}) + \mathbf{R}(t_{j-1}) - 2\mathbf{R}(t_j)}{(\Delta t)^2} . \quad (11)$$

The existence of an effective potential implies that the radial part $a_R(t_j)$ of the relative acceleration is a function of $R(t_j)$ only, so that, reporting in a graph the pairs $(R(t_j), a_R(t_j))$, the points should be distributed on well defined curves. This is exhibited by Figure 4, where such points are reported for three trajectories, in which the ion was found to remain stable for the whole integration time, i.e. for times of the order of picoseconds. The points are seen to lie on pretty well defined curves, so that in each case there exists a function $f(R)$ (depending parametrically on the initial data), such that

$$a_R = \frac{1}{\mu} f(R) \quad (12)$$

where μ denotes the reduced mass of the protons. Then, taking a primitive $V(R)$ (with changed sign) of the function $f(R)$, one gets

$$a_R = -\frac{1}{\mu} \partial_R V(R) . \quad (13)$$

Now, the figure shows that the three curves are evidently different, depending on the chosen initial data. But this had to be expected because, according to perturbation theory, the effective potential depends not only on the protons distance, but also on the values of the adiabatic invariants of the electronic hamiltonian.

We thus decided to integrate the equations of motion for several initial data chosen in a suitable way, i.e., by keeping fixed both the initial value of R and the electronic state, while changing only the kinetic energy of the protons. Indeed, in such a way one is assured that the value of each integral of motion of the electronic system with clamped protons is the same for all such trajectories. As one sees in Fig. 5, which refers to three such trajectories, the points defined by all pairs $(R(t_j), a_R(t_j))$ of the trajectories, are apparently located on a single pretty well defined curve. Then the potential $V(R)$ can be determined by integrating numerically, as a function of R , the values μa_R

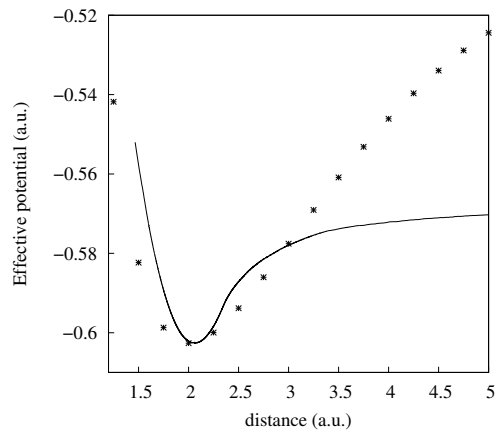


Figure 6: Effective potential as a function of proton distance, computed for initial data more generic than the one chosen in Figure 1 (continuous line), together with the quantum potential in the Born-Oppenheimer approximation (stars). Distance and potential are given in atomic units (a.u.).

found: actually this obviously determines the potential up to an additive constant.

We now describe the results for the potential, starting from those obtained for initial data of “generic type”, i.e., leading to motions in which the electron continues to bounce from one proton to the other. A typical form of the effective potential thus found is exhibited in Figure 6. The initial data for the electron were chosen as follows: the energy E was fixed at the experimental value, while the value l of the component of the angular momentum p_φ along the inter-nuclear axis was set equal to 0.6. In this way one is assured that the electronic hamiltonian with clamped potential, as shown in Figure 3, is essentially integrable. Then we find that there exists a value for the “third integral” (i.e., one of the “invariant curves” exhibited in the upper panel of the figure), such that the equilibrium distance is equal to the experimental one. The additive constant was chosen in such a way that the minimum of the effective potential coincide with the minimum of the Born-Oppenheimer quantum potential.

From the qualitative point of view the result might be considered satisfactory, since it exhibits that a binding effect exists in a classical frame. Quantitatively, however, the result is not so good, because not only the quantum potential is not well reproduced, but also the vibrational frequency is found to be about one and a half times larger than the experimental one. One should thus perform a systematic exploration of the possible electronic states, in order to check whether a better agreement with the experimental data can be found, which we didn’t do. We only observed that the result just illustrated is the best one in a neighborhood of the particular state considered, because larger values of the oscillation frequency were always found.

However, following an old suggestion advanced by Langmuir in [18] and particularly by Urey in [28], it occurred to us to find that there exist electronic states in a different region which lead to results that are apparently much better, the best of which is reported in Figure 1. We considered in fact, as the mentioned authors, electronic motions in the equatorial - or median - plane. (i.e. the plane of symmetry for the ions, normal to the inter nuclear axis). The electronic state was chosen in order to fit the experimental values of the bond length and of the vibrational frequency of the protons, i.e., the quadratic part of the potential. Instead, startlingly, as can be seen in Figure 1, the effective potential obtained is seen to actually fit the quantum one not only in the linear regime (in terms of which the initial data had been selected), but also in an extended nonlinear one. However, while in the case

of Figure 6, the ion was stable with respect to changes of the initial data in an open domain, in the latter case (motion on the equatorial plane) the ion turns out to be stable only for initial electron velocities in the equatorial plane and for protons' initial velocities along the inter nuclear axis. Otherwise the ion splits into a proton and a hydrogen atom. In the case of Figure 1, the electronic angular momentum along the inter nuclear axis was given the value 0.96 (i.e. essentially equal to \hbar , since we are using atomic units), whereas the energy was taken equal to $E = -0.89$.

We finally end this section with a short description of the integration method, which is indeed standard in stellar dynamics simulations, and we actually took from the Ref. [20]. As was already pointed out, during its motion the electron can come very close to any of the two protons and thus, in order to keep the precision of the numerical integration, the integration step has to be reduced. But this is likely to prejudice the symplectic character of the integration algorithm. To avoid this, in the above cited paper it was proposed to regularize the equations of motion by using, in place of the time t , the variable s defined by

$$ds \stackrel{\text{def}}{=} \frac{dt}{U} , \quad (14)$$

U being the potential energy of the system. In such a way it turns out that to equal increments of the variable s correspond time increments which are very small near the singular points of the potential, where it diverges. After the change of variable the equations of motion preserve the hamiltonian form, with the only difference that, instead of the original hamiltonian $H = T + U$, where T and U are the kinetic and the potential energies, the hamiltonian now takes the form

$$H' \stackrel{\text{def}}{=} \log(T - E) + \log(-U) , \quad (15)$$

where E is the value of H determined by the initial data. The only difference is that for the kinetic energy T of the electron we used the relativistic formula; moreover in U there appears a repulsive part which obviously doesn't show up in the case of stellar dynamics. However one easily checks that, if the total energy E is negative, the potential U remains negative, and thus the hamiltonian H' turns out to be well defined. The equations of motion were integrated using the leap-frog algorithm (which is well known to be symplectic), whereas t was obtained by computing the definite integral $\int_0^t U ds$ through the trapezoidal rule.

4 Conclusions

It seems to us that the most relevant result emerging from the present study is that in atomic physics the use of newtonian trajectories, normally employed for the ions, can *in principle* be extended to electrons, at least in the simplest possible case involving just one electron, which occurs for the H_2^+ ion. Indeed, in such a case it was found that initial data exist which lead to trajectories that present a chemical bond, reproducing pretty well experimental data such as the bond length and the protons' vibrational frequency, albeit not the dissociation energy. Moreover, the corresponding effective potential can actually be computed, being qualitatively (but only partially, quantitatively) similar to the quantum one.

A further interesting point concerns the role of the relativistic correction that had to be introduced in the model, in order to take into account the high velocities of the electron. This has a great impact, as the unperturbed reference system of clamped protons loses its integrable character, so that it presents a coexistence of regular and strongly chaotic domains in phase space. Consequently the binding effect exists only in the sufficiently regular domains, and these, for generic motions, turn out to be realistic domains in which the electron trajectories have angular momentum larger than an action of the order of the reduced Planck constant \hbar .

These are concrete dynamical properties of the relativistic extension of the standard classical model of the H_2^+ ion, and to have established them constitutes the actual contribution of our work.

This having been ascertained one may then ask how well can experimental phenomena such as bond length, ions' vibrational frequency and dissociation energy be reproduced. And the provisional answer indicated here seems to be: two out of the three, with many problems remaining open. Our hope is that some further physical feature may be found, analogous to the relativistic correction introduced here, that may allow at the same time to overcome the qualitative difficulty met in dealing with more than one electron, and the quantitative difficulties still met in dealing with the H_2^+ ion.

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