# New adiabatic invariants in the problem of two H atoms which are far apart

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The asymptotic behavior of the terms of the hydrogen molecule as the internuclear distance goes to infinity, $R\to\infty$, is analyzed. The effective Hamiltonian of the dipole approximation generates a completely integrable dynamics on a simplectic manifold $S^2\times S^2\times S^2\times S^2$. New expressions for the integrals of motion are derived. The spectrum of the effective Hamiltonian is studied.

New experimental capabilities and several applications of Rydberg states in various branches of physics and technology have recently attracted much more research interest to the Rydberg states of atoms and molecules.[1] From the theoretical standpoint, the most interesting entities are Rydberg systems with two electrons, since they are useful for studying such fundamental phenomena as electron–electron correlations and also since they are relatively simple systems, which are amenable to theoretical analysis on the basis of fairly realistic models.

Our purpose in the present study was to learn about a system of two excited hydrogen atoms which are separated by a large distance $R$. Specifically, we assume that $R$ is much larger than the dimensions of the Coulomb orbits of the electrons. We also assume that the conditions for the applicability of the adiabatic approximation hold, and we carry out the entire analysis at frozen value of $R$. A distinctive feature of this problem is that the multiple degeneracy of the Coulomb spectrum makes the motion of the electrons highly correlated even at large internuclear distances $R$ (large with respect to the doubly excited states of the hydrogen molecule; Refs. 2 and 3, for example).

Interestingly, despite the exceeding complexity of the classical trajectories, the dynamics is completely integrable in the dipole approximation. This fact (which has not previously been recognized) is of fundamental importance for a systematic classification of the levels. Specifically, it allows one to introduce a complete set of good quantum numbers which classify the (collective) electron states of the system. In the way of applications of this problem we should mention a calculation of the asymptotic behavior of the terms of the $H_2$ molecule in the limit $R\to\infty$ and also the problem of two impurity Coulomb centers. For simplicity we restrict the discussion below to the case of hydrogen Rydberg atoms. The effective Hamiltonian found by taking an average over the fast (Coulomb) phase shifts is

$$H_{eff}=\frac{9n_1n_2}{4R^3}\left(\mathbf{A}_1\cdot\mathbf{A}_2-3(\mathbf{A}_1\cdot\vec{\nu})(\mathbf{A}_2\cdot\vec{\nu})\right)\equiv\frac{9n_1n_2}{4R^3}\mathcal{H}, \tag{1}$$

where $\mathbf{A}_{1,2}$ are the Runge-Lenz vectors of the electrons. We will use lower-case letters for the operators and also the quantum numbers corresponding to the first electron, while we will use upper-case letters for the second electron.

The dynamic variables are the vector orbital angular momenta of the electrons, $\mathbf{l}$ and $\mathbf{L}$, and the Runge-Lenz vectors $\mathbf{a}$ and $\mathbf{A}$, which satisfy the commutation relations of the $SO(4)\oplus SO(4)$ algebra:

$$\mathbf{l}\cdot\mathbf{a}=\mathbf{L}\cdot\mathbf{A}=0,\qquad \mathbf{l}^2+\mathbf{a}^2=n^2,\qquad \mathbf{L}^2+\mathbf{A}^2=N^2\,. \tag{2}$$

The Casimir functions which are fixed by relations (2) single out orbits $Q(n,N)$ of the dynamic symmetry group $SO(4)\times SO(4)$ of the form $S^2_{n/2}\times S^2_{n/2}\times S^2_{N/2}\times S^2_{N/2}$ ($S^2_r$ is a two-dimensional sphere of radius $r$) with the natural structure of a simplectic manifold specified by a Kirillov-Constant-Surieau form. To prove the exact integrability of a dynamic system with Hamiltonian (1), it is sufficient, by virtue of the Liouville theorem, to find four integrals which are in involution. We will do this by the Lax method, following the paper by Perelomov *et al.*,[4] which generalizes Manakov's results[5] (Manakov used the Dubrovin theorem[6] to prove the exact integrability of the dynamics of an $N$-dimensional solid) to the case of two interacting $N$-dimensional solids. We switch from Hamiltonian's equations, which have the form of Euler's equations on the algebra $SO(4)\oplus SO(4)$, to the Lax matrix equation $\mathbf{L}=[\mathbf{M},\mathbf{L}]$. In constructing the Lux representation, we will ignore limitations (2) on the dynamic variables for a moment and consider the dynamics on the entire algebra $SO(4)\oplus SO(4)$, but not on the orbit $Q(n,N)$. Directing the $z$ axis along the internuclear axis, and following the prescription of Ref. 4, we find the following ansatz for the matrices $L$ and $M$, which form an $L$–$A$ pair:

$$L(\lambda)=\left(\begin{array}{c|c} k & i\lambda a \\ \hline i\lambda\alpha & K\end{array}\right),\qquad M(\lambda)=\left(\begin{array}{c|c} b & i\lambda\beta \\ \hline i\lambda\beta & B\end{array}\right),$$

where $k_{ij}=l_{ij}$, $k_{i4}=a_i$, $k_{ij}=L_{ij}$, $k_{i4}=A_i$, $b_{ij}=B_{ij}=0$, $b_{i4}=-\alpha_iA_i$, $B_{i4}=-\alpha_ia_i\,(i,j=1,2,3)$, $\alpha=\mathrm{diag}(1,1-1/2,0)$, $\beta=\mathrm{diag}(0,0,0,1)$.

All the integrals of motion can be found as coefficients of the expansion $\mathrm{tr}(L(\lambda))^{2k}$ $(k=1,..,4)$ in the spectral parameter $\lambda$. The space $Q(n,N)$ has a natural simplectic structure, induced from the algebra $SO(4)\oplus SO(4)$. Since a simplectic form on $Q(n,N)$ is nondegenerate, $Q(n,N)$ is a simplectic manifold. This circumstance makes the Liouville theorem applicable.

We turn now to a calculation of the integrals of motion. We denote by $I_{2k,r}$ the coefficient of $\lambda^r$ in the expansion of $\mathrm{tr}(L(\lambda))^{2k}$ in powers of $\lambda$. The four integrals $I_{2,0}$, $I_{4,0}$, $I_{6,0}$ and $I_{8,0}$ are combinations of Casimir functions and are fixed by conditions (2). We are left with the six nontrivial integrals $I_{4,2}$, $I_{6,2}$, $I_{6,4}$, $I_{8,2}$, $I_{8,4}$ and $I_{8,6}$, four of which are functionally independent. Actually, two of these integrals are already known. These are Hamiltonian (1) itself and the projection of the total angular momentum onto the internuclear axis, $J=(\mathbf{l}+\mathbf{L},\vec{v})$. Here are explicit expressions for the other integrals:

$$J_2=\frac{1}{4}(\mathbf{a}^2+\mathbf{A}^2)+\frac{3}{4}(\mathbf{a}\cdot\vec{v})^2+(\mathbf{A}\cdot\vec{v})^2+(\mathbf{l}\cdot\mathbf{L})-\frac{3}{2}(\mathbf{l}\cdot\vec{v})(\mathbf{L}\cdot\vec{v}),$$

$$J_3 = ((\mathbf{l}\cdot\mathbf{L}) - \frac{3}{2}(\mathbf{l}\cdot\vec{\nu})(\mathbf{l}\cdot\vec{\nu}))^2 - \mathbf{l}^2\mathbf{L}^2 + ((\mathbf{a}\cdot\mathbf{A}) - \frac{3}{2}(\mathbf{a}\cdot\vec{\nu})(\mathbf{A}\cdot\vec{\nu}))^2$$

$$- ((\mathbf{l}\cdot\mathbf{A}) - \frac{3}{2}(\mathbf{l}\cdot\vec{\nu})(\mathbf{A}\cdot\vec{\nu}))^2 - ((\mathbf{a}\cdot\mathbf{L}) - \frac{3}{2}(\mathbf{a}\cdot\vec{\nu})(\mathbf{L}\cdot\vec{\nu}))^2$$

$$- \frac{3}{4}(\mathbf{a}^2\cdot\mathbf{A}^2 + \mathbf{a}^2((\mathbf{L}\cdot\vec{\nu})^2) - (\mathbf{A}\cdot\vec{\nu})^2) + ((\mathbf{l}\cdot\vec{\nu})^2 - (\mathbf{a}\cdot\vec{\nu})^2)\mathbf{A}^2) .$$

Making use of the circumstance that the simplectic manifold of the problem is a Kähler manifold, we can write the quantization condition as the requirement that a characteristic class of quantum stratification be positive.[7] We restrict the discussion to the case in which the orbits of the electrons are highly elongated along the internuclear axis, i.e., the case $(\mathbf{a},\vec{v}) \sim n$, $(\mathbf{A},\vec{v}) \sim N$. It turns out that for this class of states the spectrum of the operator $\mathscr{H}$ is approximately harmonic $\mathscr{H} \approx -2nN + 2nN(\omega_1 s_1 + \omega_2 s_2)$ where $\omega_{1,2}^2 = \frac{1}{2}(1/n^2 + 1/N^2) \pm [(1/n^2 + 1/N^2)^2 - 3/n^2N^2]^{1/2}$, and $s_{1,2}$ are the principal quantum numbers of the oscillators. As the points $\mathscr{H} = \pm nN$ are approach, the spacing between levels decreases. These points correspond to logarithmic singularities in the density of states, which stem from the topological restructuring of the trajectories near singularities of the equipotential surface (crudely speaking, these singularities are of the nature of four-dimensional saddles). In the interval $\mathscr{H} \in (-2nN, -nN) \cup (nN, 2nN)$, the states have a spontaneous dipole moment, which could be observed experimentally. The polarizability of this system is related to the density of states by a known equation (Ref. 8, for example).


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