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An effective potential method for the calculation of hydrogen molecule ion energy in a strong magnetic field

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Using the adiabatic approximation and adiabatic variational approximation with an effective potential, the total energies and the equilibrium internuclear separations of H_2^+ ion in states $\sigma_g, \pi_u, \delta_g, \phi_u, \gamma_g, \eta_u$ in strong magnetic fields have been calculated. Our results reproduced those obtained by Vincke and Baye (Vincke M and Baye D 1985 *J. Phys. B: At. Mol. Phys.* **18** 167), which are considered the most reliable. We found a basic function with better convergence than the Landau functions.

Keywords: strong magnetic field, effective potential method, hydrogen molecule ion, adiabatic variational approximation

PACC: 3120, 3260

1. Introduction

During the past 30 years the influence of a strong magnetic field on the properties of an atom or molecular system has been studied in a number of articles.[1−4] Most investigations dealt with hydrogen molecule ion and only a few works of essentially qualitative character dealt with few-electron molecules.

A detailed understanding of the behaviour of the H_2^+ ion in a strong magnetic field is of fundamental interest; it will give us a general idea of the effects of an external field on the chemical bond. As examples of such effects, already observed for the ground state of the H_2^+ ion, we mention the contraction of the bond length, the increase of the dissociation energy with increasing magnetic field strength, and the changes in the topology of the electronic potential-energy surfaces.

Many sophisticated calculations with respect to the energy E_{R_0}, the equilibrium internuclear separation R_0, the dissociation energy $E_{\rm D}$, the adiabatic potential curves, the vibrational energies, and the energy correlation diagrams of the H_2^+ ion in strong magnetic fields have been made. The methods adopted mainly include adiabatic approximation,[5] variational approximation,[6] the atomic orbital method[7] and the Monte Carlo method,[8] etc. In the above-mentioned methods, adiabatic approximation can be applied to the extremely high field regime only; when magnetic field strength decreases, the accuracy of the results decreases. Variational approximations are based on special choices of variational electronic wavefunctions which take into account the symmetry lowering due to the presence of the external magnetic field. They are only applicable to the one-electron problem and in each case are restricted to a certain range of field strength. The atomic orbital method requires very large memory for calculation, so it is difficult to apply it to many-electron problems. In Ref.[9] a new method using adiabatic approximation and variational principle and introducing an effective potential has been applied to the hydrogen atom in a strong magnetic field. Now we apply this method to hydrogen molecule ion in a strong magnetic field.

This paper is organized as follows: section 2 gives the theory; section 3 gives the numerical method and results; and a conclusion is given in section 4.

2. Theory

In order to reduce the three-body problem to a quantum-mechanical one-electron problem, for simplicity, we use the strict Born–Oppenheimer approximation throughout, where the nuclear coordinates are fixed. We presume that the molecular axis of the H_2^+

ion aligns along the direction of an applied magnetic field. Taking the z-axis parallel to the direction of the uniform magnetic field H and putting two nuclei of the H_2^+ ion on the z-axis at a distance $2R$ from each other, we take the midpoint between the two nuclei as the origin. Using a cylindrical coordinate system (z, ρ, ϕ) in atomic units (length and energy in units of Bohr radius and Rydberg), the strength of magnetic field is measured by $\beta = B/B_0 (B_0 = 2.3505 \times 10^5 \mathrm{T})$, the Hamiltonian of the H_2^+ ion is expressed as

$$\hat{H}(\rho, z, \phi) = -\left[\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial}{\rho}\right) + \frac{1}{\rho^2}\frac{\partial^2}{\partial\phi^2} + \frac{\partial^2}{\partial z^2}\right] + \beta(\hat{l}_z + \hat{s}_z) + \frac{\beta^2\rho^2}{4} - \frac{2}{r_A} - \frac{2}{r_B} + \frac{1}{R}, \quad (1)$$

where r_A and r_B are the distances of the electron from nuclei $A(z = R)$ and $B(z = -R)$, respectively. The Schrödinger equation is

$$\hat{H}(\rho, z, \phi)\,\bar{\Psi}(\rho, z, \phi) = E\overline{\Psi}(\rho, z, \phi). \quad (2)$$

Writing the total wavefunction as $\overline{\Psi}(\rho, z, \phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}\,\Psi(\rho, z)$ (where m is the azimuthal quantum number), we obtain the equation that $\Psi(\rho, z)$ satisfies

$$\hat{H}(\rho, z)\,\Psi(\rho, z) = E\,\Psi(\rho, z), \quad (3)$$

in which the two-dimensional Hamiltonian is

$$\hat{H}(\rho, z) = -\frac{\partial^2}{\partial\rho^2} - \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{m^2}{\rho^2} + \frac{\beta^2\rho^2}{4} + \beta(m + 2m_s) - \frac{\partial^2}{\partial z^2} - \frac{2}{\sqrt{\rho^2 + (z-R)^2}} - \frac{2}{\sqrt{\rho^2 + (z+R)^2}} + \frac{1}{R}. \quad (4)$$

Since the Hamiltonian includes the Coulomb potential, equation (3) now has no analytic solutions. Many approximations have been used, e.g. the adiabatic approximation which neglects this Coulomb interaction part and solves the analytic eigenfunctions of ρ direction (Landau functions Φ_{nm}). Then the wavefunction can be expressed as

$$\Psi(\rho, z) = F(z)_{m\nu}\,\Phi(\rho)_{0m}, \quad (5)$$

where ν denotes the number of nodes in the z-direction. Since the Landau function $\Phi_{nm}(\rho)$ neglects the effect of the Coulomb potential completely, when β decreases (i.e. Coulomb interaction increases correspondingly), the precision of the results decreases. To overcome this difficulty, recently by using variational principle under adiabatic approximation we have derived adiabatic variational equations. We write the two-dimensional trial wavefunction $\Psi(\rho, z)$ as

$$\Psi(\rho, z) = \Phi(\rho)F(z) \quad (6)$$

and introduce a functional of total energy

$$\overline{H} = \langle\Psi|\hat{H}|\Psi\rangle = \langle\Phi|\hat{H}_\rho|\Phi\rangle + \langle F|\hat{H}_z|F\rangle + \langle\Phi F|V_{\mathrm{eff}}|\Phi F\rangle + \frac{1}{R}, \quad (7)$$

where

$$\hat{H}_\rho = -\frac{\partial^2}{\partial\rho^2} - \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{m^2}{\rho^2} + \frac{\beta^2\rho^2}{4} + \beta(m + 2m_s),$$

$$\hat{H}_z = -\frac{\partial^2}{\partial z^2},$$

$$V_{\mathrm{eff}} = -\frac{2}{\sqrt{\rho^2 + (z-R)^2}} - \frac{2}{\sqrt{\rho^2 + (z+R)^2}}.$$

Considering Φ and F vary infinitesimally and retaining its normalization, we leave the functional $\overline{H}$ stationary, that is

$$\partial\overline{H} - E_\rho\partial\langle\Phi|\Phi\rangle - E_z\partial\langle F|F\rangle = 0.$$

So we can establish two equations (adiabatic variational equations):

$$[\hat{H}_\rho + \langle F|\hat{V}_{\mathrm{eff}}(\rho, z)|F\rangle]\Phi(\rho) = E_\rho\Phi(\rho), \quad (8)$$

$$[\hat{H}_z + \langle\Phi|\hat{V}_{\mathrm{eff}}(\rho, z)|\Phi\rangle]F(z) = E_z f(z). \quad (9)$$

The total energy is expressed as

$$E = \langle\Psi|\hat{H}|\Psi\rangle = E_\rho + E_z - \langle\Psi|\hat{V}_{\mathrm{eff}}|\Psi\rangle + \frac{1}{R}. \quad (10)$$

The corresponding boundary conditions are

$$\Phi(\rho)\underrightarrow[\rho\to 0]{}\rho^{|m|} \quad \Phi(\rho)\underrightarrow[\rho\to\infty]{}\rho^{|m|}\exp(-\rho^2\beta/4), \quad (11)$$

$$F_{m\nu}(z)\underrightarrow[z\to 0]{}\begin{cases}\cos\left(\sqrt{E - V_{\mathrm{eff}}(z)}z\right) \\ (\nu = \text{even number}), \\ \sin\left(\sqrt{E - V_{\mathrm{eff}}(z)}z\right) \\ (\nu = \text{odd number}),\end{cases} \quad (12)$$

$$F_{m\nu}(z)\underrightarrow[z\to\infty]{}(-1)^\nu\exp\Big(-\sqrt{(-2E)}|z|\Big). \quad (13)$$

Equations (8) and (9) can be solved by the self-consistent field method. The results are better than those of the adiabatic method, but it requires much more CPU time. In this paper, we use an improved method. We introduce an effective potential including the parameter λ

$$\hat{V}(\rho) = -\frac{4}{\sqrt{\rho^2 + \lambda}} \quad (14)$$

to replace

$$\left\langle F\left| -\frac{2}{\sqrt{\rho^2+(z-R)^2}}-\frac{2}{\sqrt{\rho^2+(z+R)^2}}\right|F\right\rangle,$$

for simplicity. This corresponds to rewriting the Hamiltonian as

$$\hat{H}(\rho,z)=\hat{H}_\rho+\hat{H}_z+\hat{W}(\rho,z)+\frac{1}{R},$$

in which

$$\hat{H}_\rho=-\frac{\partial^2}{\partial\rho^2}-\frac{1}{\rho}\frac{\partial}{\partial\rho}+\frac{m^2}{\rho^2}+\frac{\beta^2\rho^2}{4}+\beta(m+2m_s)+\hat{V}(\rho),$$

$$\hat{H}_z=-\frac{\partial^2}{\partial z^2},$$

$$\hat{W}(\rho,z)=-\frac{2}{\sqrt{\rho^2+(z-R)^2}}-\frac{2}{\sqrt{\rho^2+(z+R)^2}}-\hat{V}(\rho).$$

First we solve the eigenfunctions of $\hat{H}_\rho$

$$\hat{H}_\rho\Phi(\rho)=E_\rho\Phi(\rho). \tag{15}$$

Then substituting $\Psi(\rho,z)=\Phi(\rho)F(z)$ into Eq.(3), we have

$$[\hat{H}_z+\hat{W}(z)]F(z)=E_zF(z), \tag{16}$$

in which

$$\hat{W}(z)=\left\langle\Phi\left|-\hat{V}(\rho)-\frac{2}{\sqrt{\rho^2+(z-R)^2}}-\frac{2}{\sqrt{\rho^2+(z+R)^2}}\right|\Phi\right\rangle. \tag{17}$$

The total energy can be expressed as

$$E=E_\rho+E_z+\frac{1}{R}. \tag{18}$$

Equations (15) and (16) are new adiabatic variational equations given by this paper. The corresponding boundary conditions are the same as those of Eqs.(11)–(13).

3. Numerical method and results

Equations (15) and (16) can be solved by the Runge–Kutta method, the eigenvalues and eigenfunctions can be determined using the matching method. The parameter λ is determined by a variational minimization of total energy E. We use quadratic interpolation to find the minimum value of E.

In Tables 1–6, we present the results (3) of this paper for states σ_g,π_u,δ_g,ϕ_u,γ_g and η_u of H_2^+ ion in strong magnetic fields ($10\le\beta\le1000$). The present results are compared with the adiabatic variational results (1), the adiabatic approximation results (2) and the results of Vincke and Baye (*)[6] which are obtained by the most elaborate method using 81 base functions.

Table 1. Energy and equilibrium internuclear separations of σ_g state ($m=0,\nu=0$) of H_2^+ ion in strong magnetic fields ($10\le\beta\le1000$).

β (B/B_0)	$E(1)$ /Ryd	$E(2)$ /Ryd	$E(3)$ /Ryd	λ	$E(*)$ /Ryd	$2R(1,3)$ /a.u.	$2R(2)$ /a.u.	$2R(*)$ /a.u.
10	–4.3070	–4.1078	–4.2981	0.0302	–4.3346	0.956	1.039	0.950
20	–5.6096	–5.4513	–5.6041	0.0192	–5.6383	0.762	0.803	0.756
50	–7.9307	–7.8151	–7.9280	0.0104	–7.9608	0.563	0.578	0.559
100	–10.2470	–10.1569	–10.2452	0.0066	–10.2777	0.448	0.456	0.446
200	–13.1506	–13.0812	–13.1492	0.0042	–13.1808	0.359	0.362	0.357
500	–18.0673	–18.0180	–18.0663	0.0024	–18.0949	0.270	0.272	0.269
1000	–22.7466	–22.7070	–22.7458	0.0016	–22.7694	0.220	0.221	0.219

Table 2. Energy and equilibrium internuclear separations of π_u state ($m=-1,\nu=0$) of H_2^+ ion in strong magnetic fields ($10\le\beta\le1000$).

β (B/B_0)	$E(1)$ /Ryd	$E(2)$ /Ryd	$E(3)$ /Ryd	λ	$E(*)$ /Ryd	$2R(1,3)$ /a.u.	$2R(2)$ /a.u.	$2R(*)$ /a.u.
10	–2.6981	–2.6594	–2.6974	0.0863	–2.6842	1.528	1.569	1.510
20	–3.6030	–3.5705	–3.6026	0.0517	–3.5916	1.174	1.195	1.164
50	–5.2340	–5.2090	–5.2338	0.0265	–5.2239	0.835	0.842	0.827
100	–6.8859	–6.8662	–6.8858	0.0161	–6.8773	0.651	0.654	0.645
200	–8.9871	–8.9726	–8.9870	0.0099	–8.9806	0.510	0.512	0.506
500	–12.6154	–12.6036	–12.6154	0.0052	–12.6084	0.375	0.376	0.373
1000	–16.1305	–16.1215	–16.1305	0.0033	–16.1246	0.300	0.300	0.299

Table 3. Energy and equilibrium internuclear separations of δ_g state ($m = -2, \nu = 0$) of H_2^+ ion in strong magnetic fields ($10 \leq \beta \leq 1000$).

β	$E(1)$	$E(2)$	$E(3)$	λ	$E(*)$	$2R(1,3)$	$2R(2)$	$2R(*)$
(B/B_0)	/Ryd	/Ryd	/Ryd		/Ryd	/a.u.	/a.u.	/a.u.
10	–2.1477	–2.1315	–2.1476	0.1387	–2.1305	1.906	1.934	1.880
20	–2.8912	–2.8772	–2.8912	0.0823	–2.8738	1.449	1.463	1.428
50	–4.2421	–4.2309	–4.2421	0.0416	–4.2251	1.018	1.023	1.006
100	–5.6222	–5.6129	–5.6222	0.0250	–5.6058	0.786	0.788	0.778
200	–7.3919	–7.3843	–7.3919	0.0151	–7.3764	0.611	0.612	0.608
500	–10.4745	–10.4689	–10.4745	0.0078	–10.4604	0.444	0.466	0.443
1000	–13.4919	–13.4875	–13.4919	0.0048	–13.4789	0.353	0.353	0.352

Table 4. Energy and equilibrium internuclear separations of ϕ_u state ($m = -3, \nu = 0$) of H_2^+ ion in strong magnetic fields ($10 \leq \beta \leq 1000$).

β	$E(1)$	$E(2)$	$E(3)$	λ	$E(*)$	$2R(1,3)$	$2R(2)$	$2R(*)$
(B/B_0)	/Ryd	/Ryd	/Ryd		/Ryd	/a.u.	/a.u.	/a.u.
10	–1.8458	–1.8368	–1.8458	0.1871	–1.8270	2.205	2.225	2.216
20	–2.4957	–2.4878	–2.4957	0.1105	–2.4763	1.667	1.676	1.630
50	–3.6828	–3.6764	–3.6828	0.0552	–3.6634	1.162	1.166	1.144
100	–4.9024	–4.8970	–4.9024	0.0331	–4.8835	0.892	0.894	0.881
200	–6.4747	–6.4701	–6.4747	0.0120	–6.4565	0.691	0.692	0.686
500	–9.2312	–9.2276	–9.2312	0.0101	–9.2141	0.499	0.499	0.497
1000	–11.9470	–11.9438	–11.4970	0.0062	–11.9307	0.395	0.395	0.393

Table 5. Energy and equilibrium internuclear separations of γ_g state ($m = -4, \nu = 0$) of H_2^+ ion in strong magnetic fields ($10 \leq \beta \leq 1000$).

β	$E(1)$	$E(2)$	$E(3)$	λ	$E(*)$	$2R(1,3)$	$2R(2)$	$2R(*)$
(B/B_0)	/Ryd	/Ryd	/Ryd		/Ryd	/a.u.	/a.u.	/a.u.
10	–1.6475	–1.6418	–1.6475	0.2315	–1.6281	2.458	2.472	2.404
20	–2.2341	–2.2291	–2.2341	0.1368	–2.2138	1.851	1.858	1.802
50	–3.3098	–3.3056	–3.3098	0.0684	–3.2892	1.285	1.287	1.258
100	–4.4195	–4.4159	–4.4195	0.0409	–4.3992	0.983	0.984	0.971
200	–5.8558	–5.8526	–5.8558	0.0243	–5.8361	0.758	0.759	0.750
500	–8.3861	–8.3833	–3.3861	0.0124	–8.3672	0.545	0.545	0.543
1000	–10.8913	–10.8883	–10.8913	0.0075	–10.8727	0.429	0.429	0.428

Table 6. Energy and equilibrium internuclear separations of η_u state ($m = -5, \nu = 0$) of H_2^+ ion in strong magnetic fields ($10 \leq \beta \leq 1000$).

β	$E(1)$	$E(2)$	$E(3)$	λ	$E(*)$	$2R(1,3)$	$2R(2)$	$2R(*)$
(B/B_0)	/Ryd	/Ryd	/Ryd		/Ryd	/a.u.	/a.u.	/a.u.
10	–1.5042	–1.5002	–1.5042	0.2367		2.681	2.694	
20	–2.0441	–2.0406	–2.0441	0.1615		2.013	2.019	
50	–3.0373	–3.0343	–3.0373	0.0801		1.392	1.394	
100	–4.0652	–4.0626	–4.0652	0.0481		1.063	1.064	
200	–5.3998	–5.3975	–5.3998	0.0287		0.818	0.818	
500	–7.7599	–7.7577	–7.7599	0.0145		0.586	0.587	
1000	–10.1054	–10.1029	–10.1054	0.0086		0.460	0.460	

As shown in Tables 2–5, our total energies for the states π_u, δ_g, ϕ_u and γ_g are lower than those estimated by Vincke and Baye[6] by $(0.03-1.1)\%$. This means that our wavefunctions for those states are more precise than those of Vincke and Baye. However those differences show a decreasing trend with the decrease of $|m|$ and increase of β; for example, $0.49\%, 0.18\%, 1\%$, and 1.1% for π_u, δ_g, ϕ_u, and γ_g states at $\beta = 10$, and $0.03\%, 0.09\%, 0.1\%$ and 0.17% for π_u, δ_g, ϕ_u, and γ_g states at $\beta = 1000$, respectively. We can also see that our present results are in good agreement with those of the adiabatic variational method, especially for higher β or bigger $|m|$.

In Table 1 we can see that our total energies for the δ_g state are higher than those obtained by Vincke and Baye by $(0.842-0.1)\%$, and the results of the adiabatic approximation are higher than those obtained by Vincke and Baye by $(5.2 - 0.27)\%$. This means that our results for the δ_g state are better than those of the adiabatic approximation but worse than those of Vincke and Baye. We can also see that our present results for the δ_g state are less precise than those of the adiabatic variational method.

4. Conclusion

The precision of our present method can be compared with that of the adiabatic variational method and the method of Vincke and Baye. But our method has the advantage of using less CPU time than the other methods, and we need not estimate the form of the wavefunctions in advance, so it can easily be applied to many-electron systems.

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