

CORRELATION, RELATIVISTIC AND ADIABATIC CORRECTIONS TO THE GROUND STATE POTENTIAL CURVE OF THE HYDROGEN MOLECULE

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Received March 13, 2000

Accepted July 14, 2000

Dedicated to Professor Ludovít Treindl on the occasion of his 70th birthday.

Correlation, relativistic and adiabatic corrections are computed for the electronic ground state of the hydrogen molecule for $r \leq 12$ a.u. In contrast to previous calculations (based on the numerical solution of the Schrödinger equation, mainly done by Wolniewicz *et al.*), our results are based on the ordinary *ab initio* treatment using a four-component wave function with fully relativistically reoptimized basis sets and adiabatic corrections by the treatment developed in our laboratory. The calculated energies are fitted to the polynomial/exponential analytical function and the evaluated spectroscopic parameters are compared with those obtained in the same manner from the Wolniewicz data. The results presented show a good agreement with exact numerical calculations published previously.

Key words: Relativistic corrections; Adiabatic corrections; Hydrogen; *Ab initio* calculations; Wave function; Potential energy curve.

The accurate potential energy curve for the ground state of the hydrogen molecule computed 40 years ago by Kolos and Roothaan¹ has been improved several times for various regions of the internuclear distance by the Wolniewicz group²⁻⁶ using a very general expansion of the wave function. All recent calculations trying to account for the relativistic and adiabatic corrections were based on the very general multiterm form of the variational wave function and the subsequent numerical solution of the Schrödinger equation. They showed that the inclusions of both relativistic and adiabatic corrections are of great importance for a reasonable agreement with experimental data.

This work was undertaken in order to evaluate the correlation, relativistic and adiabatic corrections to the ground state potential energy curve of the

hydrogen molecule with an accuracy comparable with the Wolniewicz numerical results⁵, and strictly based on the ordinary *ab initio* treatment with Gaussian basis set expansion of the wave function. The potential energy curve has been evaluated for the same internuclear distance region as reported by Wolniewicz⁵.

THEORETICAL

Relativistic corrections have been calculated by solving the Dirac–Hartree–Fock equations with a four-component wave function^{7–9} based on the Gaussian basis set expansion with fully relativistic reoptimized expansion coefficients and exponents¹⁰. It has been shown¹⁰ that the use of original nonrelativistic basis sets (exponents as well as expansion coefficients) may lead to incorrect results even if additional primitives with larger exponents are added. This solution has been used for the following inclusion of correlation effects. As the hydrogen molecule contains two electrons only, the SD-CI expansion provides full CI results. All relativistic and CI calculations were performed using the four-component molecular relativistic package MOLFDIR (ref.¹¹).

The hydrogen basis set adopted in all the presented relativistic calculations was obtained by the optimization procedure using the numerical atomic relativistic program package GRASP (ref.¹²). More details about this optimization method can be found in ref.¹⁰. In order to obtain the basis sets sufficiently large and costly appropriate, we first optimized the primitive Gaussian basis sets exponents using the stochastic optimization treatment and then refined them by the ordinary gradient energy-functional based procedure, adopting the Gaussian sphere model for the nucleus. We optimized 10s primitive Gaussian functions for neutral H atom. Then, additional functions with higher angular momenta (p, d, f) have been added. Since the relativistic effects influence mainly the electrons near the nucleus, we used the original nonrelativistic basis set for describe higher angular momenta p, d, f. These additional functions were used as uncontracted. The final basis set used was of 10s5p4d1f quality (Table I). The primitive basis sets for small components of the Dirac wave functions were generated by the kinetic balance. The relativistic contraction scheme used in our calculations is presented in Table I.

In our previous paper¹³ dealing with the calculation of adiabatic corrections, we showed that the Born–Handy formula^{14,15}, accounting for the adiabatic corrections to the energy, can be reformulated at the level of the routinely used coupled perturbed Hartree–Fock (CPHF) method¹⁶, and ex-

pressed over the derivatives of the expansion coefficients in a compact form. This enables us to decompose the adiabatic correction into the parts associated with the vibrational and rotational/translational components of the nuclear motion. This procedure was actually used here for an approximate inclusion of adiabatic corrections to the ground state energies. Be-

TABLE I
Exponents and coefficients of relativistic hydrogen Gaussian basis functions

Function	Orbital	Exponent	Coefficient
s	1	1 683.122107	0.000046931
		251.284883	0.000364777
		57.353057	0.001900121
		16.339164	0.007867807
		5.3694243	0.027584960
		1.9509730	0.082718485
		0.7655929	0.203094564
		0.3191116	0.361535575
		0.1389537	0.355963414
		0.0611333	0.103814608
	2	1.9509730	1.0
	3	0.7655929	1.0
	4	0.3191116	1.0
p	5	0.1389537	1.0
	6	0.0611333	1.0
	1	8.6490000	1.0
	2	3.4300000	1.0
	3	1.3600000	1.0
d	4	0.5390000	1.0
	5	0.2140000	1.0
	1	4.4530000	1.0
	2	1.9580000	1.0
	3	0.8610000	1.0
f	4	0.3780000	1.0
	1	1.2000000	1.0

cause of the small magnitude of these corrections (tenths and hundredths of cm^{-1}), we calculated the adiabatic corrections within the nonrelativistic ground state wave function (by our estimations, the error in comparison with the use of the relativistic ground state wave function should be less than 1%).

The quality of the computed energies has been examined by the rigorous least square fit¹⁷ to the analytical function of the following form

$$E(r) = \sum_{k=0}^5 A_k \zeta^k \exp\left(\sum_{l=1}^2 B_l \zeta^l\right), \quad \text{where } \zeta = (r - r_e)/r. \quad (1)$$

Such a form of the potential energy function obeys all the necessary limit physical conditions¹⁸. The spectroscopic parameters (r_e , ω_e , $\omega_e x_e$, B_e , α , D_e) were obtained from the derivatives of the function (1) in the minimum.

RESULTS AND DISCUSSION

The total energy E_{tot} (including relativistic, correlation and adiabatic corrections), total energy without adiabatic correction $E_{\text{DHF+SDCI}}$ (relativistic DHF energy with SDCI correlation energy contribution), ΔE_{rel} (net relativistic correction), ΔE_{ad} (net adiabatic correction) and ΔE_{W} (absolute difference between our and Wolniewicz energies) are listed in Table II. The net relativistic corrections ΔE_{rel} were obtained as the differences between relativistic and nonrelativistic energies (obtained with the same relativistic DHF code applying the condition for the speed of light $c \rightarrow \infty$ and with the same Gaussian basic set). For the sake of simplicity, we used the same internuclear distances as reported by Wolniewicz⁵. Even though we used only a moderate Gaussian basis set for the hydrogen atoms, one can see from Table II that our DHF SCF energies corrected for the correlation and adiabatic effects show satisfactory agreement with data of Wolniewicz⁵. The absolute mean error is approximately 0.6 mhartree. One can also compare individual corrections to the total energy (relativistic and/or adiabatic).

The quality of the calculated hydrogen potential energy curve can be demonstrated by the calculation of spectroscopic parameters. Since they depend on the higher derivatives of the potential energy function, they are very sensitive to the shape of the curve. All calculated spectroscopic parameters are listed in Table III. For comparison, the experimental data¹⁹ are also presented. Spectroscopic parameters for the Wolniewicz energies⁵ have

been obtained in the same manner as for our potential energy curve. Because we restricted ourselves to the spectroscopic parameters containing at most the fourth derivative of energy (first anharmonic constant $\omega_e x_e$), also a comparison of spectroscopic parameters for the best numerical values of Wolniewicz⁵ with the experimental parameters shows small differences. The importance of the adiabatic correction is readily seen from Table III. Its

TABLE II

Total DHF + SDCI energies ($E_{\text{DHF+SDCI}}$), relativistic corrections (ΔE_{rel}), adiabatic corrections (ΔE_{ad}), total corrected energies ($E_{\text{tot}} = E_{\text{DHF+SDCI}} + \Delta E_{\text{ad}}$), and the differences between our and Wolniewicz's numerical results⁵ (ΔE_{W}). All values in a.u.

r	$E_{\text{DHF+SDCI}}$	$\Delta E_{\text{rel}} \cdot 10^5$	$\Delta E_{\text{rel}} \cdot 10^5$ Ref. ⁵	$\Delta E_{\text{ad}} \cdot 10^4$	$\Delta E_{\text{ad}} \cdot 10^4$ Ref. ⁵	E_{tot}	$\Delta E_{\text{W}} \cdot 10^4$ Ref. ⁵
0.90	-1.08311910	-2.510	-1.687	5.993	6.244	-1.08251985	-5.158
1.00	-1.12401839	-2.195	-1.500	5.724	5.985	-1.12344597	-5.102
1.10	-1.14953708	-1.942	-1.357	5.482	5.755	-1.14898887	-5.065
1.20	-1.16441449	-1.739	-1.246	5.264	5.552	-1.16388806	-5.044
1.30	-1.17182485	-1.572	-1.161	5.069	5.375	-1.17131797	-5.032
1.35	-1.17344045	-1.501	-1.126	4.979	5.295	-1.17294258	-5.028
1.40	-1.17395150	-1.436	-1.096	4.893	5.221	-1.17346215	-5.024
1.45	-1.17353203	-1.377	-1.069	4.813	5.152	-1.17305075	-5.017
1.50	-1.17232947	-1.323	-1.045	4.736	5.089	-1.17185582	-5.008
1.60	-1.16805734	-1.229	-1.006	4.596	4.976	-1.16759774	-4.981
1.70	-1.16193304	-1.151	-0.977	4.470	4.881	-1.16148601	-4.943
1.80	-1.15454410	-1.085	-0.955	4.358	4.804	-1.15410831	-4.895
2.00	-1.13761583	-0.981	-0.931	4.168	4.696	-1.13719907	-4.736
2.20	-1.11962400	-0.906	-0.926	4.016	4.643	-1.11922239	-4.547
3.00	-1.05690765	-0.761	-1.015	3.674	4.831	-1.05654020	-3.131
5.00	-1.00367734	-0.740	-1.291	3.620	5.410	-1.00331530	0.577
6.00	-1.00079081	-0.764	-1.320	3.710	5.437	-1.00041978	1.146
8.00	-1.00005376	-0.803	-1.330	3.856	5.445	-0.99966818	1.438
10.00	-1.00001669	-0.822	-1.331	3.933	5.446	-0.99962337	1.459
12.00	-1.00001259	-0.830	-1.331	3.966	5.446	-0.99961597	1.447

inclusion in both our and Wolniewicz data represents roughly the same effect, so that the absolute error of harmonic frequency is less than 1 cm^{-1} . The discrepancy in the dissociation energy can be partly explained by the fact we approximated the energy $E(r \rightarrow \infty)$ by the last tabulated value in the Wolniewicz paper⁵ $E(r = 12 \text{ a.u.})$. Although it seems theoretically unjustified, we used this assumption in order to minimize the errors in the process of interpretation of our results. For the Wolniewicz data, this makes the absolute error of $7 \cdot 10^{-4} \text{ eV}$ (6 cm^{-1}). The worst estimated parameter obtained from our hydrogen potential energy curve is the dissociation energy (about 0.016 eV less than the experimental value). The origin of this discrepancy lies in the fact we used insufficient expansion of the Gaussian basis functions but the procedure used for estimation of dissociation energy may also play a certain role.

CONCLUSIONS

The aim of this study was to compare the precise four-component relativistic *ab initio* calculation of the ground-state potential energy of the hydrogen molecule including the correlation and adiabatic corrections with the best numerical data. Hydrogen molecule was used since, as the best theoretically described molecular system, it plays an important role as a testing ground for many theoretical and experimental methods. Our ambitions were not to reproduce comprehensively the best theoretical results, but to show that it is also possible to approach them satisfactorily in the frame-

TABLE III
Calculated and experimental spectroscopic parameters

Quantity	This paper ^a	Wolniewicz ^{a,b}	This paper ^c	Wolniewicz ^{b,c}	Experiment ^d
$r_e \cdot 10^{10}, \text{ m}$	0.74141	0.74143	0.74165	0.74163	0.74144
$\omega_e, \text{ cm}^{-1}$	4 403.70	4 403.50	4 401.40	4 401.89	4 401.21
$\omega_e x_e, \text{ cm}^{-1}$	121.89	121.60	121.83	121.49	121.33
$B_e, \text{ cm}^{-1}$	60.854	60.851	60.816	60.818	60.853
$\alpha_e, \text{ cm}^{-1}$	3.037	3.032	3.034	3.029	3.062
$D_e \cdot 10^4, \text{ cm}^{-1}$	4.65	4.65	4.64	4.64	4.71
$D_0^0, \text{ eV}$	4.4625	4.4767	4.4613	4.4774	4.4781

^a Without adiabatic corrections; ^b ref.⁵; ^c including adiabatic corrections; ^d ref.¹⁹.

work of the HF treatment with the Gaussian basis set expansion. The results fulfilled our expectations, showing a sufficient agreement with the best numerical data available in literature. For a better agreement it will be the subject of some experimentation to adopt larger basis set expansions and a more sophisticated procedure for estimation of the dissociation energy. However, investigations of the Polish group²⁰⁻²³ showed that the use of explicitly correlated Gaussian functions as a basis set for a better agreement with the Wolniewicz data is desirable.

The work has been funded by the Slovak Grant Agency (project No. 1/7388/20).

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