**Ab initio calculations with a nonspherical Gaussian basis set: Excited states of the hydrogen molecule**

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A basis set of generalized nonspherical Gaussian functions (GGTOs) is presented and discussed. As a first example we report on Born-Oppenheimer energies of the hydrogen molecule. Although accurate results have been obtained, we conclude that \( H_2 \) is too "simple" to allow for a substantial gain by using nonspherical functions. We rather expect that these functions may be particularly useful in calculations on large systems. A single basis set of GGTOs was used to simultaneously calculate the potential energy curves of several states within each subspace of \( ^1\Sigma_u^+ \) symmetry. We hereby considered the entire region of internuclear distances \( 0.8 \leq R \leq 1000 \) a.u. In particular the results for the fourth up to sixth electronic states show a high accuracy compared to calculations which invoke explicitly correlated functions, e.g. the relative accuracy is at least of the order of magnitude of \( 10^{-3} \) a.u. Energies for the \( ^4\Sigma_u^+ \) and \( ^4\Sigma_g^- \) were improved and accurate data for the \( ^6\Sigma_u^+ \), \( ^6\Sigma_g^+ \), and \( ^6\Sigma_u^+ \) state are, to the best of the authors knowledge, presented for the first time. Energy data for the seventh up to the ninth electronic state within each subspace were obtained with an estimated error of the order of magnitude of \( 10^{-4} \) a.u. The \( ^7\Sigma_u^+ \) and the \( ^6\Sigma_u^+ \) state were found to exhibit a very broad deep outer well at large internuclear distances.

I. INTRODUCTION

The usual method to obtain a molecular wavefunction is to expand this wavefunction in terms of products of linear combinations of atomic orbitals respecting the spatial and spin symmetries and the Pauli principle. In order to limit the computational expense a fast convergence of the calculation is desirable. The convergence essentially depends on the choice of the atomic basis set. Slater-type functions (STOs) and Gaussian-type functions (GTOs) hereby have gained large acceptance in quantum chemistry. Since computer evaluation of three- and four-center integrals over STO basis functions is very time consuming, Boys\(^{7}\) proposed in 1950 the use of GTOs instead of STOs. For GTOs the integral evaluation requires much less computer time than for STOs. This results from the fact that three- and four-center integrals over GTOs may be reduced to two-center-integrals.

The slow convergence of the calculations is the major drawback of using GTOs. On the one hand, GTOs provide a poor description of the desired cusp of atomic orbitals for electrons located near the nucleus and the correlation cusp for small interelectronic distances. On the other hand, GTOs are not well suited for describing electronic states with distorted wavefunctions, e.g. for states involving high angular momenta. As a consequence, a linear combination of several GTOs is necessary for an accurate representation of such a wavefunction.

A possible way of convergence improvement is to explicitly include the interelectronic distance in the wavefunction which was introduced by Hylleraas\(^{7}\) for the helium atom. For the hydrogen molecule the use of confocal elliptical coordinates was introduced by James and Coolidge\(^{7}\) and proved to be very efficient. Further development on the latter method was done by Kolos and Wolniewicz (see e.g. Refs. \( ^{7,8} \) for accurate ground state energies) which lead to theoretical energies for low lying electronic states of the hydrogen molecule with spectroscopic accuracy. However, the use of basis sets with confocal orbitals is restricted to diatomic molecules and cannot be used in polyatomic calculations.

Recently, a basis set of generalized GTOs\(^{7}\) was introduced for calculations in the presence of external magnetic fields. This basis set of generalized (nonspherical) Gaussian functions (GGTOs) proved to be an excellent choice for calculations in strong magnetic fields. The flexibility of the basis functions allows for an adaption of the basis functions to the symmetry of the electronic wave function of the molecule which made the new GGTOs superior to simple GTOs or STOs. In the presence of an external magnetic field the wavefunction is, depending on the field strength, distorted towards a cylindrical symmetry. The obtained results for calculations on \( H_2^+ \) and \( H_2^2 \) in the presence of magnetic fields (see Refs. \( ^{7,8} \) and references therein) are very encouraging. This motivated the present authors to raise the question whether this basis set may be also useful for calculations in field free space. The first part of this paper deals with the presentation of the basis set and discusses briefly the possible advantages GGTOs may have in calculations on large systems. In the second part of this paper we report on a simple example: the investigation...
of the electronic structure of the hydrogen molecule using GGTOs. A detailed knowledge of this simplest diatomic molecule is of fundamental interest in different branches of chemistry and physics. Fundamental molecular processes can be studied, as, for example, charge exchange processes in $H^+ + H^-$ collisions, associative ionization reactions $H + H^+ \rightarrow H + H^++e^-$, excitation reactions $H(1s) + H(1s) \rightarrow H(1s) + H(2s)$ or $H(1s) + H(2p)$ or chemical exchange processes $H + H_2 \rightarrow H_2 + H$. For a detailed understanding of the above mentioned processes one first needs accurate electronic energies for the hydrogen molecule. The investigations dealing with electronic states of $H_2$, both experimentally and theoretically, are too numerous to be mentioned here. For an overview of experimental studies we refer the reader to Refs. 2, 3 and references therein. In particular we mention an experiment recently reported by Reinhold et al. the outer minimum of the third excited $\Sigma^+_g$ state was investigated. For theoretical data on the electronic structure of $H_2$ see Refs. 2, 3, 4, 5, 6 and references therein.

In the present investigation, a full CI approach is used to obtain the $n\Sigma^-_{g,u} n = 1 - 9$ electronic states. Particular emphasis was put on accurate results for the first five excited states within each subspace of $\Sigma$ symmetry, e.g. the $n\Sigma^-_{g,u} n = 2 - 6$ states. Our aim was to compute all of these states covering the entire range of internuclear distances from $R = 0.8 \text{a.u}$ to $R = 1000 \text{a.u}$ with a single basis set of GGTOs. In the present investigation we report on accurate Born-Oppenheimer energies of the third, fourth and fifth excited $\Sigma^+_u$ and $\Sigma^+_g$ states and of the fifth excited $\Sigma^+_g$ state. Born-Oppenheimer energies for the third excited $\Sigma^+_g$ state have been given by Dressler and Wohlecks. These results were obtained with the aid of a basis set not optimized for the state in question and could be further improved. Excited $\Sigma^+_g$ states were investigated by Borondo et al. but only with a very small basis set of GTOs and at a few selected internuclear distances. To the best of the authors knowledge Born-Oppenheimer energies of the $5\Sigma^+_u$, $6\Sigma^+_u$ and $6\Sigma^+_g$ states are presented here for the first time. The results on the other $n\Sigma^+_g n = 1 - 6 H_2$ electronic states are compared with the best data found in the literature. As a side product of our calculations we obtained electronic energies for the $n\Sigma^+_g n = 7 - 9$ states which have not been investigated up to now. These states are shown graphically but no energy data are provided.

II. GENERALIZED GAUSSIANS

The present computations were done with a basis set of generalized GTOs which has been originally introduced in order to perform calculation in the presence of an external magnetic field. In the most general appearance the basis functions in Cartesian coordinates read as follows:

$$\phi_n (r; \alpha, R, C) = \exp \left[ -iA(C)r \right] (x - R_x)^{n_x} (y - R_y)^{n_y} (z - R_z)^{n_z} \times \exp \left[ -(r - R)^T \alpha (r - R) \right]$$

$$r = (x, y, z)^T$$

denotes the vector of the electronic coordinates and $R = (R_x, R_y, R_z)^T$ is the position vector characterizing the center of the orbital. $A(C)$ ist the vector potential at the position $C$, where $C$ is a vector of variational parameters which are determined by minimizing the expectation value of the energy. The gauge factor $\exp \left[ -iA(C)r \right]$ ensures the approximative gauge invariance of the energy expectation values. For our calculation on the $H_2$ molecule in the absence of a magnetic field this phase factor vanishes. For a detailed discussion of the dependence of energy expectation values on the choice of gauge we therefore refer the reader to Ref. 7. Without the additional gauge factor needed in the presence of a magnetic field this type of basis functions was first introduced by Singer. The matrix

$$\alpha = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix}$$

is a real symmetric matrix of variational parameters which had to be optimized to minimize the energy expectation value.

Basis functions of type (1) possess several advantages compared to GTOs. In order to describe wave functions which differ from a pure spherical symmetry the number of basis functions may be reduced. Contrary to GTOs the flexibility of basis functions of type (1) provide the possibility for an adaption of the basis functions according to the symmetry of the molecule being investigated. Therefore a more rapid convergence with increasing size of the basis set in energy calculations is expected when dealing with wavefunctions which significantly differ from a spherical symmetry. The GGTO basis set can also be useful in calculations involving effects as angular correlation. If GTOs are used this leads, in particular for larger systems which involve high angular momenta, to a strong increase in the size of the basis set. In that situation the use of GGTOs might be very useful: As a consequence of the nonspherical shape, simple GGTOs contain portions of several different angular momenta and may therefore reduce the number of
GTOs with high angular momenta significantly. Despite the obvious advantages of the GGTO basis compared to the GTO basis a main drawback is the evaluation of the matrix elements: The use of the GGTO basis requires a numerical integration in the evaluation of three- and four-center matrix elements. Hereby three-center matrix elements can be fastly evaluated but the evaluation of four-center matrix elements is time consuming. Consequently, for larger systems a combination of GTOs and GGTOs seems to be useful. For a description of core and other localized electrons GTOs are well suited since possible anisotropies in the wavefunction are small. GGTOs should be taken for a description of outer electrons and the electrons participating in the chemical bond and/or in those cases where angular correlation effects are relevant.

As an example we considered the ground state of \( H_2 \) \( 1^1\Sigma_g^+ \) with a total energy at the equilibrium distance of \(-1.1744757 \text{ a.u.}\)\(^7\) and investigated the influence of the anisotropy of the basis function with the aid of a \((6s,3p,2d,1s)\) basis set. The energy was obtained by an optimization of the parameters for the GTO and GGTO basis at the CI level for \( H_2 \). For the GTO basis we obtained an energy of \(-1.174006 \text{ a.u.}\) at the equilibrium distance. The use of anisotropic basis functions lead to an improved energy of \(-1.174086 \text{ a.u.}\) The definition of the anisotropy \( a \) is as follows: Let \( \alpha_{xx} \leq \alpha_{zz} \), so \( a := 1 - \frac{\alpha_{zz}}{\alpha_{xx}} \). The anisotropy for s-type functions is pretty small, e.g., between 0.01 and 0.05. However it increased for functions involving angular momenta not equal zero — for these type of functions anisotropies up to 0.35 were calculated. Compared to the GTO basis, the use of GGTOs yielded 17\% of the remaining energy to the exact result.

III. POTENTIAL ENERGY CURVES OF \( H_2 \)

For an investigation of the electronic structure of the hydrogen molecule the basis functions in Eq. \(1\) can be simplified significantly. Due to the cylindrical symmetry of the molecule we choose all off-diagonal elements of the matrix to be zero and in addition \( \alpha_{xx} = \alpha_{yy} \). In this work we used only orbitals centered at the positions of the nuclei. The origin of our coordinate system coincides with the midpoint of the internuclear axes and the protons are located on the z-axis. Therefore, the basis functions used in the present investigation read as follows:

\[
\phi_n(r; \alpha_{xx}, \alpha_{zz}, \pm R/2) = x^{n_x} y^{n_y} \left( z \mp R/2 \right)^{n_z} \exp \left\{ -\alpha_{xx} \left( x^2 + y^2 \right) - \alpha_{zz} \left( z \mp R/2 \right)^2 \right\},
\]

(3)

For a detailed description of the evaluation of the various matrix elements needed in the computation of the wavefunction using this particular type of basis functions we refer the reader to Ref. 7.

In the present study Born-Oppenheimer energies were calculated for the lowest nine states within each of the \( \Sigma \) subspaces, e.g., for both singlet and triplet as well as gerade and ungerade parity. Hereby particular emphasize was put on accurate results for the \( n^1\Sigma_g^+, n = 2 - 6 \) states. A single basis set of GGTOs has been used for all states and internuclear distances. The determination of the electronic potential energy curves (PECs) was done by the following procedure: Since we would like to perform calculations for a large range of internuclear distances, i.e. for 0.8 a.u. < \( R < 1000 \) a.u., we had to ensure obtaining correct energies in the dissociation limit. Therefore, several GGTOs were optimized for electronic states of atomic hydrogen and included in the basis set. Second, a limited number of basis functions for the description of angular correlation was optimized at a CI level at selected internuclear distances. Following this procedure we arrived at a number of approximately 3800 two particle functions at the full CI level of expansion. Most of these function were needed for the correct description of the dissociative behaviour. The anisotropies in the s-type functions varies drastically. S-type functions involving high parameter values (corresponding to electrons located near the nucleus) show an almost negligible anisotropy but functions with small parameter values (necessary for the description of higher excited states) possess anisotropies up to 1. Basis functions describing angular correlation may possess even larger distortions. In our calculations the maximum of distortion was found to be 3.

In spite of the larger convergence error for energies of the \( n^1\Sigma_g^+, n = 7 - 9 \) states we graphically show the PECs for these states. The relative error in the dissociation limit varies between \( 10^{-4} \) and \( 10^{-6} \) and is estimated to be of the order of magnitude of \( 10^{-7} \) in the vicinity of the equilibrium internuclear distance. Our results represent the first \textit{ab initio} data for these excited states. The results allow us, in particular, to demonstrate the interaction of the attractive \( H^+ + H^- \) states with \( H(1s) + H(\text{nl}) \) states at very large internuclear distances. For this purpose a large regime of internuclear distances is necessary. The electronic energies were calculated at 480 different internuclear distances in the interval 0.8 a.u. < \( R < 1000 \) a.u. A complete table of the results can be obtained from the authors upon request. The accuracy with respect to the energy data obtained in our investigation for states up to the fifth excited ones is estimated to be typically of the order of magnitude of \( 10^{-4} \) for \( 1^1\Sigma_g^+ \) and \( 10^{-5} \) to \( 10^{-6} \) for the \( n^1\Sigma_g^+, n = 2 - 6 \) and \( n^3\Sigma_g^+, n = 1 - 6 \) states, respectively. The position of minima and maxima were determined with an accuracy of \( 10^{-2} \) a.u. of the internuclear distance.
A. The $^1\Sigma_g^+$ subspace

Many calculations have been performed on Born-Oppenheimer states within the $^1\Sigma_g^+$ subspace. Very accurate energies for the ground state ($^1\Sigma_g^+$) are given in Ref. 7 and the lowest five excited states were considered in Ref. 7. A very detailed theoretical investigation of the $^4\Sigma_g^+$ was recently done by Wolniewicz1 in order to explain the experimental results by Reinhold et.al.7 The calculations mentioned above served as a benchmark in the determination of the accuracy of our data. Our aim is the study of excited $H_2$ states and the data concerning the ground state of the hydrogen molecule is only a side product and less accurate than that for excited states. At the equilibrium internuclear distance of the ground state we obtained an energy of 1.1742937 a.u. which implies an accuracy of 1.82 $\times$ 10$^{-4}$ a.u. Our data for the n $^1\Sigma_g^+$ n = 2 - 6 states are in general at least as accurate as 5 $\times$ 10$^{-5}$ a.u. or, equivalently, $\approx$ 11 cm$^{-1}$ compared to the results of Refs. 7, 7. For some internuclear distances our calculations for higher excited states, e.g. the $4\Sigma_g^+$ and $5\Sigma_g^+$ state, yield energies slightly lower than those given in Ref. 7. The maximum difference in energy amounts to 4.229 cm$^{-1}$ at $R = 2.00$ a.u. ($E = -0.63490478$ a.u.) for the $4\Sigma_g^+$ and 11.551 cm$^{-1}$ at $R = 2.80$ a.u. ($E = -0.61390242$ a.u.) for the $5\Sigma_g^+$ state, respectively. These results indicate that a more accurate investigation of these excited states is still possible which can be done by an optimization of the wavefunction for these particular states.

The PECs for the n $^1\Sigma_g^+$ n = 4 - 9 states are shown in Fig. 1. In general we depict excited states up to the fifth one with solid and higher excited states with dotted lines. The figure nicely demonstrates the series of avoided crossings between the corresponding $H(1s) + H(nl)$ Heitler-London configuration with the $H^+ + H^-(1s)^2$ ion-pair configuration. The total ionic energy can be written as

$$E_{ion}(R) = -0.527751014 - \frac{1}{R} \frac{211.897}{(2R)^2}$$

(4)

The corresponding PEC was also included in Fig. 1. For the $4\Sigma_g^+$ state its Born-Oppenheimer curve and the PEC of $H^-$ was found to be very close7 for internuclear distances $20 \leq R \leq 35.7$. The difference between higher excited states and the PEC of $H^-$ was not investigated up to now. The PEC of the $7\Sigma_g^+$ state is for some range of internuclear distances also very close to the PEC of $H^-$. In particular we mention that the $7\Sigma_g^+$ state exhibits a very broad deep outer well with a total energy at the minimum of 0.555487 a.u. at large internuclear distances due to the interaction with the $H^+ + H^-(1s)^2$ configuration. The depth of this well, e.g. the difference between the maximum at $R = 8.7$ a.u. and the minimum at $R = 33.7$ a.u. approximately amounts to 0.015473 a.u. A series of avoided crossings leads to the energetically equal dissociation limits of the n $^1\Sigma_g^+$ n = 7 - 9 states. The dissociation limit of the $10\Sigma_g^+$ state is the $H^+ + H^- (1s)^2$ ion-pair configuration.

B. The $^1\Sigma_u^+$ subspace

For a reference of the most accurate data on the electronic energies of the four lowest states of $^1\Sigma_u^+$ symmetry we used the results given by Dressler and Wolniewicz2. In that investigation energies of the three lowest $^1\Sigma_u^+$ states were presented with high accuracy. Our results show a relative accuracy of the order of magnitude of 10$^{-4}$ for the lowest and 10$^{-5}$ for the first and second excited state. Energies for the $4\Sigma_u^+$ state however, were obtained in Ref. 7 with the aid of a wavefunction optimized for the three lowest states. Therefore, these results are not optimal and can be improved. Table 1 lists our first time results on energy data for the fourth, fifth and sixth excited $^1\Sigma_u^+$ state at a few selected internuclear distances and a comparison of the present results with that of Ref. 7 is given in Tab. 1. From Tab. 1 we observe that a substantial improvement of the energy data of Ref. 7 was possible at relevant internuclear distances. Hereby the most significant improvement of previous results (54.87 cm$^{-1}$) was obtained in the vicinity of the (first) internuclear equilibrium distance at $R = 2.00$ a.u. The PECs of the n $^1\Sigma_u^+$ n = 3 - 9 states are graphically shown in Fig. 2. Similarly to the $^1\Sigma_g^+$ subspace we recognize the existence of two deep outer wells at large internuclear distances. As in the case of the $^1\Sigma_g^+$ subspace this results from avoided crossings with the $H^+ + H^- (1s)^2$ configuration. For the $3\Sigma_u^+$ state the existence of a second outer minimum was first predicted by Dabrowski and Herzberg2 and theoretically shown by Kolos2. Our calculations revealed a broad and deep outer well of the $6\Sigma_u^+$ state which is located at 33.7 a.u. and possesses a total energy of $-0.555492$ a.u. The depth of the well, e.g., the difference between the second minimum and the maximum of the $6\Sigma_u^+$ state amounts to 0.015134 a.u.
C. The $3\Sigma^+_g$ subspace

Detailed investigations of triplet states can be found for instance in Refs. 3-5. Recently energy data for triplet states of $H_2$ for small internuclear distances were calculated by Liu and Hagstrom 6 using full CI and large elliptical basis sets. The results given by Liu and Hagstrom 7 and Kolos 8 served as the benchmark for our data for internuclear distances $R < 5$ a.u. and $R > 5$ a.u., respectively. First, we notice that our results for the $n^3\Sigma^+_{g,u}$ $n = 1-6$ triplet states (both gerade as well as ungerade symmetry) are roughly one order of magnitude more accurate than the corresponding singlet states, e.g. the relative accuracy is of the order of magnitude of $10^{-5}$ or $10^{-6}$. An explanation herefore is that for singlet states we deal with an electron cusp problem at $r_1 = r_2$ and therefore basis functions explicitly including the interelectronic distance should show a much faster convergence in particular at small internuclear distances. This cusp problem is absent for the triplet states. Furthermore, for triplet states correlation effects are reduced due to the Rydberg character of the states. As a consequence of our main goal - the accurate description of excited states - the basis set contains several s-type functions but only a few functions explicitly involving higher angular momenta. This further explains the better accuracy we have achieved for the triplet states.

For the four lowest $3\Sigma^+_g$ states our results show an accuracy of the order of magnitude of $10^{-6}$ in the vicinity of the equilibrium internuclear distance and in the dissociation limit and of $10^{-5}$ for intermediate internuclear distances, e.g. $5 \leq R \leq 10$ a.u. In this work we report for the first time results of accurate energies for the $6^3\Sigma^+_g$ state. The corresponding data are given in Tab. II and the PECs are shown in Fig. 3. For the $(5^3\Sigma^+_g)$ state a comparison of our results with that of Refs. 7-9 is presented in Tab. IV. For internuclear distances near the equilibrium configuration our energy data are slightly above that of Liu and Hagstrom but for larger distances slightly better than the best previous results given in Ref. 7. Figure 3 indicates that the $(7^3\Sigma^+_g)$ and $(8^3\Sigma^+_g)$ states (similar to the $(4^3\Sigma^+_g)$ and $(5^3\Sigma^+_g)$ states) are nearly degenerate near the equilibrium internuclear distance. However, the energies for higher excited states ($n = 7-9$) are not as accurate as those for the $(4^3\Sigma^+_g)$ and $(5^3\Sigma^+_g)$ states and therefore a more detailed study has to be performed in order to confirm this result.

D. The $3\Sigma^+_u$ subspace

For accurate energy data concerning the three lowest states of the $3\Sigma^+_u$ subspace we refer the reader to Refs. 7-9 and references therein. A qualitative description of the six lowest $3\Sigma^+_u$ states can also be found in the work by Borondo et.al. 7 However, in that paper energy data for the six lowest $3\Sigma^+_u$ states were obtained using a small GTO basis and the energy data is therefore amenable to drastic improvement. Our results for the three lowest $3\Sigma^+_u$ states show a typical accuracy of $10^{-6}$ compared to the best data given in Refs. 7-9. For the $3^1\Sigma^+_u$ state and some particular internuclear distances the present calculations yield energies which are several tenths of $cm^{-1}$ lower than those reported in Ref. 7. Table III lists our energy data for the $n^3\Sigma^+_u$ $n = 4-6$ states. PECs are depicted in Fig. 4. In general our results are of the order of magnitude of $10^{-3}$ or $10^{-2}$ lower than that given by Borondo 7. Again, we draw the readers attention to the series of avoided crossings originating from an interaction with an $H^+ + H^- (1s2s)$ ion pair configuration.

IV. CONCLUSIONS

In the first part of the paper we presented a basis set of generalized Gaussian type functions. This basis set is well suited for a description of distorted wave functions and angular correlation effects. $H_2$ has been investigated as a first test. For $H_2$ the basis set works well, but may not justify the larger effort involved in the use of nonspherical functions. We rather expect this type of functions to be useful in larger systems.

We investigated the $n^1,3\Sigma^+_g,u$ $n = 1-9$ electronic states of the hydrogen molecule using one single basis set of GGTOs. A broad range of internuclear distances $(0.8 < R < 1000$ a.u.) has been considered. Our main goal was the calculation of accurate Born-Oppenheimer energies for the $n^1,3\Sigma^+_g,u$ $n = 4-6$ states. For the first time we present PECs for the $n^1,3\Sigma^+_g,u$ $n = 7-9$ states. Energy data for the $4^1\Sigma^+_g$ and the $n^3\Sigma^+_u$ $n = 4-6$ were improved compared to the best data available in the literature. New accurate PECs were calculated for the $5^3\Sigma^+_u$, $6^3\Sigma^+_u$ and $6^1\Sigma^+_u$ state. The $7^1\Sigma^+_g$ and the $6^1\Sigma^+_g$ state were found to provide a second deep outer well arising due to an interaction with the diabatic $H^+ + H^- (1s)^2$ state. Similarly to the $4^1\Sigma^+_g$ these states also may contain several long lived valence states of $H_2$ in analogy to what has been discussed in Ref. 7.

FIG. 1. PECs (total energy in a.u.) for the third up to fifth (solid lines) and sixth up to eighth (dotted lines) excited $3\Sigma^+_g$ state. To guide the eye we also included the $H^+ + H^- (1s)^2$ diabatic state (dashed line).
FIG. 2. PECs (total energy in a.u.) for the second up to fifth (solid lines) and sixth up to eighth (dotted lines) excited $^1\Sigma_u^+$ state. To guide the eye we also included the $H^+ + H^-$ (1s)$^3$ diabatic state (dashed line).

FIG. 3. PECs (total energy in a.u.) for the second up to fifth (solid lines) and sixth up to eighth (dotted lines) excited $^3\Sigma_g^+$ state.

FIG. 4. PECs (total energy in a.u.) for the second up to fifth (solid lines) and sixth up to eighth (dotted lines) excited $^3\Sigma_u^+$ state.

TABLE I. Born-Oppenheimer energies $E$ of the $^1\Sigma_u^+$, $^5\Sigma_u^+$ and $^6\Sigma_u^+$ states. Dissociation energies $D$ are in cm$^{-1}$ (1 a.u. = 219474.64 cm$^{-1}$), all other quantities are in atomic units.

| R   | $E (^1\Sigma_u^+)$ | $D (^1\Sigma_u^+)$ | $E (^5\Sigma_u^+)$ | $D (^5\Sigma_u^+)$ | $E (^6\Sigma_u^+)$ | $D (^6\Sigma_u^+)$ |
|-----|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| 0.8 | -0.33576673       | -48238.074        | -0.32449461       | -50712.018        | -0.32427855       | -5424.985         |
| 1.2 | -0.56301611       | 1041.638          | -0.54932463       | -1367.529         | -0.54881235       | 3854.491          |
| 1.6 | -0.62202861       | 14665.730         | -0.61179855       | 12434.912         | -0.61081490       | 17462.477         |
| 1.8 | -0.63167582       | 16706.467         | -0.62142478       | 14456.625         | -0.62015441       | 19512.263         |
| 1.9 | -0.63545815       | 17117.397         | -0.62344232       | 14899.424         | -0.62201911       | 19921.517         |
| 2.0 | -0.63409815       | 17238.107         | -0.62441491       | 15032.966         | -0.62506986       | 20400.418         |
| 2.1 | -0.63021919       | 17135.585         | -0.62818775       | 14982.639         | -0.62207577       | 19933.953         |
| 2.2 | -0.63235117       | 16854.690         | -0.62703811       | 14737.339         | -0.62097556       | 19652.979         |
| 2.6 | -0.62246079       | 14684.003         | -0.61345778       | 12708.070         | -0.61086073       | 17472.537         |
| 3.0 | -0.60934757       | 11805.983         | -0.60104221       | 9983.167          | -0.59768853       | 14581.572         |
| 4.0 | -0.57870623       | 5680.986          | -0.57269612       | 3761.919          | -0.56675253       | 7791.905          |
| 5.0 | -0.56213226       | 1443.420          | -0.55458442       | -213.140          | -0.54930711       | 4077.994          |
| 5.6 | -0.5649852        | 2182.229          | -0.55022956       | -1168.921         | -0.54572663       | 3177.253          |
| 5.7 | -0.56571034       | 2228.718          | -0.55012760       | -1181.422         | -0.54507868       | 3035.945          |
| 5.8 | -0.56517395       | 2110.994          | -0.55025441       | -1163.466         | -0.54447672       | 2902.929          |
| 6.0 | -0.56372910       | 1793.886          | -0.55066494       | -1073.366         | -0.54341151       | 2669.143          |
| 7.0 | -0.55663828       | 676.580           | -0.55321945       | -512.716          | -0.54129338       | 2204.267          |
| 8.0 | -0.55673204       | 258.208           | -0.55465619       | -197.387          | -0.54114524       | 2171.753          |
| 10.0| -0.55589629       | 74.784            | -0.55550414       | -3.383            | -0.54036726       | 2002.988          |
| 15.0| -0.55619944       | 14.130            | -0.55558225       | 5.859             | -0.54997174       | 3236.623          |
| 20.0| -0.55557306       | 3.841             | -0.55556074       | 1.138             | -0.55281866       | 4732.676          |
| 30.0| -0.55555555       | -0.55555555       | -0.55555555       | -0.55555555       | -0.53125000       | -0.53125000       |

TABLE II. Comparison of Born-Oppenheimer energies for the $^3\Sigma_u^+$ state with data given by Dressler$^9$. Energy differences $\Delta = E(\text{Lit.}) - E(\text{present})$ are in are in cm$^{-1}$, all other quantities are in atomic units.

| R   | $E(\text{Ref. ?})$ | $E(\text{present work})$ | $\Delta$ |
|-----|-------------------|--------------------------|----------|
| 1.0 | -0.482967317      | -0.48309139              | +27.20   |
| 2.0 | -0.633848144      | -0.63409815              | +54.87   |
| 5.1 | -0.561982447      | -0.56205148              | +15.15   |
| 5.7 | -0.565729995      | -0.56571034              | -4.31    |
| 11.2| -0.555749330      | -0.55576957              | +4.44    |
| 20.0| -0.555531578      | -0.55557305              | +9.10    |
| 30.0| -0.55550107       | -0.55555355              | +11.03   |
TABLE III. Born-Oppenheimer energies $E$ of the $6 \Sigma_g^+$ states. Dissociation energies $D$ are in $cm^{-1}$, all other quantities are in atomic units.

| R   | $E(6 \Sigma_g^+)$ | $D(6 \Sigma_g^+)$ |
|-----|-------------------|-------------------|
| 0.8 | -0.52978808       | -45093.681        |
| 1.2 | -0.54971049       | 4051.610          |
| 1.6 | -0.61124180       | 17556.172         |
| 1.8 | -0.62043117       | 19573.006         |
| 1.9 | -0.6225080        | 19972.368         |
| 2.0 | -0.62276944       | 20086.196         |
| 2.1 | -0.6228292        | 19979.418         |
| 2.2 | -0.62102141       | 19702.547         |
| 2.6 | -0.61131929       | 17573.178         |
| 3.0 | -0.59856552       | 14774.050         |
| 4.0 | -0.56903655       | 8293.189          |
| 5.0 | -0.54974877       | 4060.012          |
| 6.0 | -0.54122673       | 2189.639          |
| 7.0 | -0.53619376       | 1085.031          |
| 8.0 | -0.53388710       | 578.776           |
| 10.0| -0.5321705        | 256.138           |
| 12.5| -0.53214863       | 197.226           |
| 15.0| -0.53171747       | 102.597           |
| 20.0| -0.53128098       | 6.800             |
| 30.0| -0.53125000       | 0.018             |
| $\infty$ | -0.53125000   | 0                 |

TABLE IV. Comparison of Born-Oppenheimer energies for the $5 \Sigma_g^+$ state with data given by Liu and Hagstrom\(^7\) ($R \leq 3.0$ a.u.) and Kolos\(^7\) ($R \geq 6.0$ a.u.) Energy differences $\Delta = E(Lit.) - E(\text{present})$ are in $cm^{-1}$, all other quantities are in atomic units.

| R   | E(Lit.)  | E(\text{present work}) | $\Delta$ |
|-----|----------|-------------------------|----------|
| 1.0 | -0.483282334 | -0.48328606             | +0.82    |
| 2.0 | -0.634509581 | -0.63450920             | -0.08    |
| 3.0 | -0.607932413 | -0.60792794             | -0.98    |
| 6.0 | -0.550672651 | -0.550678881             | +1.36    |
| 12.0| -0.549376938 | -0.549382559             | +1.23    |
| 20.0| -0.555171208 | -0.555206182             | +7.67    |
TABLE V. Born-Oppenheimer energies \( E \) of the \( 4 \overset{3}{\Sigma}^+ \), \( 5 \overset{3}{\Sigma}^+ \) and \( 6 \overset{3}{\Sigma}^+ \) states. Dissociation energies \( D \) are in \( \text{cm}^{-1} \), all other quantities are in atomic units.

| \( R \) | \( E (\overset{4}{3}\Sigma^+) \) | \( D (\overset{4}{3}\Sigma^+) \) | \( E (\overset{5}{3}\Sigma^+) \) | \( D (\overset{5}{3}\Sigma^+) \) | \( E (\overset{6}{3}\Sigma^+) \) | \( D (\overset{6}{3}\Sigma^+) \) |
|---|---|---|---|---|---|---|
| 0.8 | -0.33576681 | -48238.056 | -0.32612114 | -50355.035 | -0.32430141 | -50754.421 |
| 1.2 | -0.56030175 | 1041.670 | -0.55178019 | -828.598 | -0.54882094 | -1478.077 |
| 1.6 | -0.62232310 | 14653.783 | -0.61471484 | 12983.963 | -0.61081948 | 12129.030 |
| 1.8 | -0.63167611 | 16706.532 | -0.62347360 | 15103.815 | -0.6205808 | 14178.616 |
| 1.9 | -0.63454848 | 17117.468 | -0.62636467 | 15540.905 | -0.62202245 | 14587.798 |
| 2.0 | -0.63499850 | 17238.185 | -0.62701366 | 15863.242 | -0.62256394 | 14706.640 |
| 2.1 | -0.63362239 | 17133.668 | -0.62661900 | 15596.623 | -0.62207862 | 14600.126 |
| 2.2 | -0.6245157 | 16854.778 | -0.6241462 | 15332.294 | -0.62079922 | 14319.110 |
| 2.6 | -0.62246125 | 14684.104 | -0.6157539 | 13194.780 | -0.61086284 | 12138.546 |
| 3.0 | -0.60934867 | 11806.224 | -0.60259285 | 10324.678 | -0.59769020 | 9247.486 |
| 4.0 | -0.57869562 | 5078.657 | -0.57201487 | 3612.402 | -0.56886141 | 2481.348 |
| 4.8 | -0.56454828 | 1734.448 | -0.55734267 | 392.226 | -0.55131413 | 403.567 |
| 5.0 | -0.57068654 | 3320.867 | -0.55859069 | 930.909 | -0.55402538 | 335.835 |
| 5.5 | -0.57630268 | 2578.195 | -0.55473890 | 179.236 | -0.54957213 | -1313.210 |
| 6.0 | -0.56397471 | 1847.791 | -0.55382444 | -379.937 | -0.54764726 | -1735.670 |
| 7.0 | -0.55910158 | 778.262 | -0.55465050 | -196.636 | -0.54763133 | -1739.167 |
| 8.0 | -0.55678301 | 268.802 | -0.55536911 | -39.209 | -0.54789839 | -1680.555 |
| 10.0 | -0.55583534 | 61.406 | -0.55593464 | 8.319 | -0.54789291 | -1725.651 |
| 15.0 | -0.55558262 | 8.179 | -0.55535331 | -4.444 | -0.55285806 | -592.032 |
| 20.0 | -0.5556118 | 1.234 | -0.5554193 | -2.989 | -0.55519059 | -80.101 |
| 25.0 | -0.55556265 | 0.152 | -0.5554759 | -1.748 | -0.5552310 | -7.123 |
| \( \infty \) | -0.55555555 | -0.55555555 | -0.55555555 | -0.55555555 | -0.55555555 | -0.55555555 |
Fig. 1
Fig. 2
Fig. 4

-0.65
-0.61
-0.57
-0.53

E[a.u.]

R[a.u.]