Calculation of dissociating autoionizing states using the block diagonalization method: Application to $\text{N}_2\text{H}$

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Abstract. We report the calculation of preliminary potential surfaces necessary to treat dissociative recombination (DR) of electrons with $\text{N}_2\text{H}^+$. We performed multi-reference, configuration interaction calculations with a large active space for $\text{N}_2\text{H}^+$ and $\text{N}_2\text{H}$, using the GAMESS electronic structure code. Rydberg-valence coupling is strong in $\text{N}_2\text{H}$, and a systematic procedure is desirable to isolate the appropriate dissociating, autoionizing states. We used the block diagonalization method, which requires only modest additional effort beyond the standard methodology. We treated both linear and bent geometries of the molecules, with $\text{N}_2$ fixed at its equilibrium separation. The results indicate that the crossing between the dissociating neutral curve and the initial ion potential is not favorably located, suggesting that the direct mechanism for DR will be small. Dynamics calculations using the multi-configuration, time-dependent Hartree (MCTDH) method confirm this conclusion.

1. Introduction

Although nitrogen is very important in the chemistry of the interstellar medium, it cannot be directly observed. Its abundance must be inferred indirectly by detecting $\text{N}_2\text{H}^+$, which can be produced by the reaction

$$\text{N}_2 + \text{H}_3^+ \rightarrow \text{N}_2\text{H}^+ + \text{H}_2.$$  \hfill (1)

It was long assumed that the $\text{N}_2$ consumed in the reaction above was almost completely recovered by dissociative recombination (DR). The measurements of Adams et al [1] in 1990 indicated that the branching ratios in the dissociative recombination process strongly favor the $\text{N}_2 + \text{H}$ channel:

$$e^- + \text{N}_2\text{H}^+ \rightarrow \begin{cases} \text{N}_2 + \text{H} \\ \text{NH} + \text{N}. \end{cases}$$  \hfill (2)

However, in 2004 Geppert et al [2] reported measurements that the branching ratio to the $\text{NH} + \text{N}$ channel was dominant. This unexpected result cast doubt on the assumptions mentioned above and motivated additional experimental and theoretical work.
In 2007, Molek et al [3] reported a new experimental measurement of the branching ratio and concluded that the upper limit for the branching ratio to the NH + N channel was 5%. Also in 2007, Talbi [4] reported a theoretical investigation of the potential surfaces for linear \( \text{N}_2\text{H} \) and \( \text{N}_2\text{H}^+ \). She concluded that the likely outcome of dissociative recombination would be the \( \text{N}_2 + \text{H} \) channel, with \( \text{N}_2 \) in the first electronically excited state. There is now general agreement that the branching ratio to the NH + N channel is less than about 5% [5].

Talbi’s work [4, 6] has highlighted the need for further calculations to determine appropriate diabatic potential surfaces for both linear and bent geometries of the molecule. This work reports preliminary calculations of that type.

2. What is needed for a DR calculation

A detailed calculation of dissociative recombination must provide potential curves for both the initial molecular ion and the dissociating autoionizing state. The surfaces needed are illustrated in figures 1 and 2. Calculating the potential surface for the initial molecular ion (\( \text{N}_2\text{H}^+ \) in the present case) is straightforward and involves standard techniques of quantum chemistry. However, calculating the dissociating state is much more difficult because that state is embedded in the continuum of scattering states that correspond to \( \text{e}^- + \text{N}_2\text{H}^+ \).

Recent work by ourselves [7, 8] and others [9, 10] has shown that the block diagonalization method provides a very powerful technique to determine the necessary dissociating, autoionizing states of \( \text{N}_2\text{H} \). The block diagonalization method also allows us to determine the autoionization width \( \Gamma \), which is related to the probability that the electron incident on the molecular ion is captured into the dissociating state.

The principal difficulty that one encounters when trying to calculate the dissociating surface using the standard techniques of electronic structure is that the states of interest are (1) highly excited and (2) strongly mixed with other states. Multiple curve crossings occur, and it can be very difficult to isolate the desired potential surface. Before going into the details of our calculations, we will present an overview of the results that can be obtained by using the block diagonalization method to separate the desired states from the many other states that appear in a standard calculation.

Figure 3 shows the standard adiabatic curves obtained, and figure 4 shows the corresponding diabatic curves. These calculations were performed in the linear geometry, and \( R_4 \) is the distance from the hydrogen atom H to the center of mass of the \( \text{N}_2 \). The adiabatic curves exhibit multiple curve crossings; diabatization allows us to identify the appropriate dissociation channels.
Figure 3. Adiabatic potentials determined from the GAMESS electronic structure calculations without any additional analysis.

Figure 4. Diabatic potentials determined using the block diagonalization method. A vibrational wave function for the ion is also shown.

3. Block diagonalization method

The block diagonalization method [9] provides an effective technique for transforming the results of a standard electronic structure calculation into diabatic potential curves. An advantage of the method is that one can perform a conventional calculation of the desired size and accuracy and then obtain diabatic curves with comparable reliability. A second advantage is that the numerical effort for the diabatization is quite modest compared to the original calculation (which usually involves diagonalizing a very large, sparse matrix.)

The method requires extra effort in the determination of molecular orbitals (mo’s). Briefly, one must insure that the variation of the mo’s $\{\phi_i\}$ with molecular geometry is small. This result can be achieved by setting up the calculation in such a way that the adiabatic energies are invariant under a rotation of certain molecular orbitals, and then selecting an appropriate rotation at each geometry. For example, the MCSCF energies are invariant under an arbitrary rotation $U$ of the mo’s in the active space [11, 12]. One can replace a set of orbitals $\{\phi'_i\}$ optimized in an MCSCF with a new set

$$\phi_i = \sum_j U_{ij} \phi'_j,$$

and the MCSCF energies will not change. [9] pointed out that one can take advantage of this degree of freedom by choosing $U$ so that each mo in the set $\{\phi_i\}$ resembles as closely as possible a corresponding orbital in a set of “reference” orbitals. The reference orbitals are defined in a way that makes them easy to interpret and insures that they are slowly varying. We use the algorithm we previously implemented [7] based on a series of Jacobi rotations to maximize the overlap of each $\phi_i$ with the corresponding reference orbital.

The configuration interaction (CI) electronic wave function $\Psi_n$ for the $n^{th}$ state is represented as the sum of configurations $\Phi_m$, each constructed from the mo’s $\phi_i$:

$$\Psi_n = \sum_{m=1}^{N} c_{mn} \Phi_m,$$
The number of coefficients $N$ in the sum in Eq. 4 may be quite large (of order $10^6$). However, one can usually identify a small set of $N_\alpha$ configurations ($N_\alpha \sim 2-10$) that make the dominant contribution to $N_\alpha$ electronic states of interest. Then $N_\alpha$ will be the dimension of the diabatic Hamiltonian, and for the diabatization one only needs the $N_\alpha \times N_\alpha$ matrix of values $c_{mn}$ for the coefficients of the $N_\alpha$ dominant configurations in the $N_\alpha$ states of interest. We denote this matrix by $S$. The diabatic Hamiltonian matrix $H_{\text{dia}}$ can be expressed as a transformation of the diagonal matrix $E$ whose nonzero elements are the adiabatic eigenvalues $E_1, \ldots, E_{N_\alpha}$:

$$H_{\text{dia}} = T^\dagger E T,$$

where $(\dagger)$ denotes the adjoint (transpose for a real transformation), and

$$T = S^{-1} (SS^\dagger)^{1/2}.$$ (6)

This analysis of the adiabatic eigenvalues and eigenvectors is straightforward and only involves matrices of order $N_\alpha$. Since $H_{\text{dia}}$ is explicitly constructed by a unitary transformation of the matrix $E$ of adiabatic eigenvalues, the eigenvalues of the small matrix $H_{\text{dia}}$ will be exactly the same as the chosen $N_\alpha$ eigenvalues of the large matrix determined by the CI calculation. The determination of $H_{\text{dia}}$ is illustrated schematically in figure 5.

4. Electronic structure calculations

The electronic structure calculations reported here were performed using the GAMESS code [13]. The basis set included a 6-311G(d,p) on each N plus diffuse functions and a 10s4p1d basis on H; there were 69 total basis functions. Using the notation of Talbi [4] for the molecular orbitals, the orbital occupancy of the ground state of $N_2H^+$ is

$$1s_a^2 1s_b^2 (NN)^2 (SP)^2 (NH)^2 \pi_x^2 \pi_y^2 |,$$

where the vertical bar $(\cdot)$ signifies the highest orbital occupied in the ion core. The orbital occupancy of the $N_2H$ ground state is

$$1s_a^2 1s_b^2 (NN)^2 (SP)^2 (NH)^2 \pi_x^2 \pi_y^2 |(NH^*)^1.$$ (Ryd 1)

The Rydberg states of $N_2H$ have one electron in a highly excited orbital outside of the ion core:

$$1s_a^2 1s_b^2 (NN)^2 (SP)^2 (NH)^2 \pi_x^2 \pi_y^2 |(NH^*)^1 \pi_x^1 \pi_y^1 (N^N) \ldots |.$$ (Ryd 2) (Ryd 3) \ldots ;

we use a light color to indicate that orbitals such as $(NH^*)$ are not occupied. The dissociating valence states of $N_2H$ have an unoccupied core orbital:

$$1s_a^2 1s_b^2 (NN)^2 (SP)^2 (NH)^2 \pi_x^2 \pi_y^2 |(NH^*)^1 \pi_x^1 \pi_y^1.$$
Figure 6. Variation of the molecular orbitals with molecular geometry. The top row shows the antibonding NH$^*$ orbital for $R_d = 1.61$ Å, and $\theta = 0, 30, 60, \text{and } 90$ degrees. The second row shows the same orbital for $R_d = 2.46$ Å, at the same angles. The third row shows the $A'$ bonding $\pi$ orbital for $R_d = 1.61$ Å, and $\theta = 0, 30, 60, \text{and } 90$ degrees. The smooth changes in the molecular orbitals ensure that the block diagonalization process gives reliable diabatic potential curves.

The dissociating state important for DR is a linear combination of states corresponding to the two orbital occupancies given above.

We have completed multi-reference, configuration interaction (MRCI) calculations with an active space that includes the (NH), $\pi_x$, $\pi_y$, NH$^*$, $\pi_x^*$, and $\pi_y^*$ orbitals. We included single and double excitations from the active space, leading to 449,892 configurations. We typically calculated 25-85 eigenvalues and eigenvectors of the electronic Hamiltonian. These results are preliminary; final calculations will use a larger active space that includes Rydberg orbitals.

An important requirement for the block diagonal method is that the molecular orbitals vary smoothly with geometry. For most of the calculations reported here, it was sufficient to use natural orbitals determined by a preliminary CI calculation on the N$_2$H ground state. These orbitals can be determined by the GAMESS code. It was necessary to watch for “orbital swaps.” GAMESS orders the molecular orbitals according to an orbital energy; this procedure can lead to an unwanted interchange of two or more orbitals as the geometry changes. By estimating the orbital overlap between corresponding orbitals at similar geometries we were able to reorder the orbitals as necessary. In a few cases, such as small values of $R_d$, it was necessary to define reference orbitals explicitly as described in section 3. Figure 6 illustrates the smooth variation of the orbitals we used.

We primarily investigated the case in which DR leads to breaking the NH bond, so we froze the NN bond length at the equilibrium value appropriate for N$_2$H (taken to be $R_{NN} = 1.12$ Å). For this case it is convenient to use Jacobi coordinates, which are illustrated in figure 7. $R_d$ is the distance from the H atom to the center of mass of the N$_2$, and $\theta$ is the bending angle ($\theta = 0$ corresponds to a linear molecule.) One can then expand the potential surface using Legendre polynomials of even order:

$$V(R_{NN}, R_d, \theta) = \sum_{\lambda=0}^{2N} V_\lambda(R_{NN}, R_d) P_\lambda(\cos \theta)$$

We typically performed calculations for 8–11 different angles at each value of $R_d$. The calculated points are shown in figure 7. We have plotted the points as functions of $\sin^2 \theta = 1 - \cos^2 \theta$ in order to facilitate least squares fitting. A Legendre polynomial expansion with only even terms for $\lambda = 0, \ldots, 2N$ is an $N$th degree polynomial in $\cos^2 \theta$ or, equivalently, in $\sin^2 \theta$. By plotting the calculated points vs. $\sin^2 \theta$ we could assess the goodness of fit using standard polynomial fitting routines.

The curves shown in figure 7 are typically five-term polynomials (in $\sin^2 \theta$). It is clear from these curves that an exact fit to the calculated points would have additional undulations. We
prefer to have a somewhat smoother fit, because the additional variation in the calculated points is likely due to the uncertainty in selecting the optimum $\alpha$ and the most important configurations for each geometry. Because of the many curve crossings, the set of configurations that make the most important contribution is constantly changing. Note that the points most distant from the fitted curve tend to be at small values of $R_d$, where the potential is the steepest and small uncertainties are unlikely to be important.

Once the Legendre polynomial expansion coefficients in Eq. (7) have been determined for several values of $R_d$, they can easily be interpolated using splines. ($R_{NN}$ is fixed.) Then the full surface can be interpolated at arbitrary values of $R_d$ and $\theta$. The interpolated results are shown in figures 8 and 9. For both of these figures, we have plotted the energy vs. the cartesian coordinates of the H atom in the plane of the molecule ($x = R_d \cos \theta$ and $y = R_d \sin \theta$).

5. Dynamics calculations

We have performed preliminary dynamics calculations using the multi-configuration, time-dependent Hartree (MCTDH) method [14]. This method has emerged over the past few years as a very efficient procedure for numerical solutions of the time-dependent Schroedinger equation.
Figure 10. Potential curves for N$_2$H$^+$ and N$_2$H and relative cross sections for DR calculated using the MCTDH method. The dynamics calculations include the angular dependence of the potential surface but only the direct mechanism for DR. The energy scale is the same for both panels; the peak of the DR cross section occurs near an incident electron energy of 3 eV. The cross section from the direct mechanism for very low electron energies is very small.

6. Concluding remarks
We have reported preliminary large scale electronic structure calculations for the ground state of N$_2$H$^+$ and for several states of N$_2$H, including the dissociating state important for dissociative recombination. Initial dynamics calculations that include the bending of the molecule but freeze the N$_2$ bond length suggest that the direct mechanism of DR is not efficient. Further work is needed for a definitive calculation.
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References
[1] Adams N G, Herd C R, Geoghegan M, Smith D, Canosa A, Gomet J C, Rowe B R, Queffelec J L and Morais M 1991 J. Chem. Phys. 34 4852–4857
[2] Geppert W D, Thomas R, Semaniak J, Ehlerding A, Millar T J, Österdahl F, af Ugglas M, Djurić N, Paál A and Larsson M 2004 Ap. J. 609 459–464
[3] Molek C D, McLain J L, Poterya V and Adams N G 2007 Phys. Rev. A 29 1548
[4] Talbi D 2007 Chem. Phys. 332 298–303
[5] Larsson M and Orel A 2008 Dissociative Recombination of Molecular Ions (New York: Cambridge University Press)
[6] Talbi D 2009 J. Phys. Conf. Ser. 192 012015
[7] Spirko J A, Mallis J T and Hickman A P 2000 J. Phys. B: At. Mol. Opt. Phys 33 2395–2407
[8] Hickman A P, Miles R D, Hayden C and Talbi D 2005 Astron. and Astrophys. 438 31–37
[9] Pacher T, Cederbaum L S and Köppel H 1988 J. Chem. Phys. 89 7367–7381
[10] Domcke W and Woywod C 1993 Chem. Phys. Lett. 216 362–368
[11] Roos B O 1987 Adv. Chem. Phys. 69 399–445
[12] Schmidt M W and Gordon M S 1998 Ann. Rev. Phys. Chem. 49 233–266
[13] Schmidt M W, Baldrige K K, Boatz J A, Elbert S T, Gordon M S, Jensen J H, Koseki S, Matsunaga N, Nguyen K A, Su S, Windus T L, Dupuis M and Montgomery Jr J A 1993 J. Comp. Chem. 14 1347–1363
[14] Meyer H D, Gatti F and Worth G A (eds) 2009 Multidimensional Quantum Mechanics: MCTDH Theory and Applications (Weinheim: Wiley-VCH)