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Does N$_2^-$ exist? A coupled-cluster study

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Potential energy curves of the ground-state N$_2$ molecule and its doublet N$_2^-$ anion are calculated at the coupled-cluster level with single and double excitations and with noniterative triples [CCSD(T)] as well as with the multireference averaged-quadratic coupled-cluster (MR-AQCC) method. The N$_2^-$ anion is shown to be temporary and decays to its neutral parent plus a free electron at bond lengths shorter than ≈ 1.4 and larger than ≈ 2.5 Å. Thus, the N$_2^-$ anion exists within the $1.4 \leqslant R(\text{N–N}) \leqslant 2.5$ Å range at the Born–Oppenheimer approximation. © *1999 American Institute of Physics.* [S0021-9606(99)00511-5]

I. INTRODUCTION

It is well known that N$_2$ forms only temporary anion states following the interaction with incident electrons.[1] The nature of these temporary states, also referred to as compound or resonance states, has been the subject of numerous experimental and theoretical efforts.[2] It is generally believed[1] that a temporary N$_2^-$ ($^2\Pi_g$) state is responsible for low-energy resonances observed in scattering experiments. The nature of these resonances has been studied experimentally[1,2] and theoretically, both in the gas phase[3,4] and as adsorbates.[5]

A proper theoretical description of this temporary state appears to be complicated, since accurate calculations even for the ground-state potential energy surfaces (PEC) of N$_2$ present a problem due to the dissociation of the triply bonded molecule to nitrogen atoms in their high-spin ^4S ground states. Generally, a correct reproduction of the whole PEC in such a case typically requires the use of multiconfiguration (MC)[6,7] or multireference (MR) wave functions[8–10] in order to account for the static correlation.

However, it was shown[11] that the more economical single-reference coupled-cluster approach is capable of close reproduction of the multireference configuration interaction (MRCI) results for stretches of the $R(\text{N–N})$ bond length up to $\approx 2R_e$, where the dynamical correlation is more important.

The PEC of the N$_2^-$ ($^2\Pi_g$) state was computed in the vicinity of the neutral equilibrium bond length both at the Hartree–Fock (HF)[12–14] and MRCI[15] levels. These calculations have found an intersection point of the neutral and anion PECs, which indicates the formation of a N$_2^-$ state stable with respect to vertical detachment of an extra electron. Recently, Gianturco and Schneider[16] have performed MRCI calculations on the N$_2$–N$_2^-$ pair with a $12s7p/6s4p$ basis set augmented with two d-functions and one diffuse sp-shell. They found a bound portion of the N$_2^-$ curve at $1.48 \leqslant R(\text{N–N}) \leqslant 2.65$ Å, but were not able to reproduce the

autodetaching area of N$_2^-$ because this requires an inclusion of very diffuse functions into standard basis sets.[17]

The main purpose of the present work is to construct the N$_2^-$ ($^2\Pi_g$) PEC at the coupled-cluster level of theory with a large atomic natural orbital basis augmented with diffuse spd-shells. Our preliminary results for H$_2$–H$_2^-$ and N$_2$–N$_2^-$ PECs and the results of other calculations for the H$_2$–H$_2^-$[18] and HCl–HCl$^-$ PECs[19] have shown some continuation of the anion curves beyond the intersection point to the shorter bond-length region, where the anions should decay to their neutral parents and a free electron. Such continuations appear to be due to the use of finite basis sets and should not show up if a near-infinite basis is employed.

II. COMPUTATIONAL DETAILS

Our calculations have been performed with the ACES II suite of programs[20] at the coupled-cluster level with single and double excitations (CCSD)[21] and noniterative [CCSD(T)][22,23] inclusion of triple excitations. For the N$_2$ and N$_2^-$ systems at $R(\text{N–N}) = 1.7$ and 1.9 Å, we employed two multireference methods, multiconfiguration self-consistent field (MC-SCF) and a variation of multireference configura-
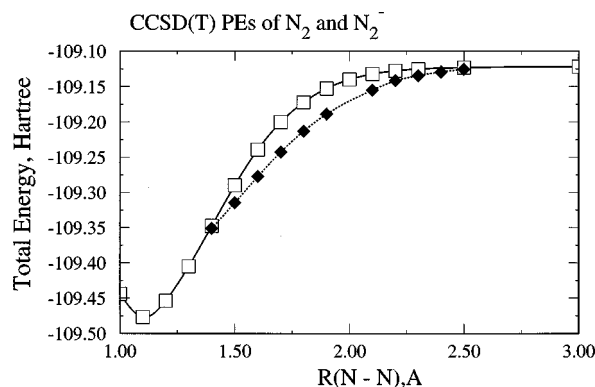

FIG. 1. CCSD(T) potential energy curves of N$_2$ ($X\ ^1\Sigma_g^+$) and N$_2^-$ ($^2\Pi_g$): the neutral molecule—open boxes, solid line; the anion—solid boxes, dotted line.

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TABLE I. Convergence of the total and orbital energies as well as the bond length of N_2^- ($^2\Pi_g$) when decreasing the exponent (ζ) of an spd-shell, sited at the middle of the N–N bond. Calculations are carried out at the CCSD+T(CCSD) (Ref. 23) level of theory. Bond length is in Å, total and orbital energies are in hartree.

Property	N_2^-, $^2\Pi_g$				N_2, $X\ ^1\Sigma_g^+$
	WMR[a]	$\zeta = 0.005$	$\zeta = 0.0005$	$\zeta = 0.00005$	WMR
$R(N–N)$	1.164 84	1.099 347	1.099 35	1.099 28	1.099 31
$E(HF)$	−108.896 380	−108.974 597	−108.989 997	−108.991 566	−108.991 948
$E(CCSD)$	−109.379 881	−109.438 332	−109.453 850	−109.455 379	−109.455 598
$E(CCSD+T)$	−109.404 934	−109.460 351	−109.475 855	−109.477 431	−109.477 606
ϵ_{XXMO}[b]	0.024 66	0.017 34	0.001 75	0.000 18	0.059 88

[a]The smallest p-exponent is 0.034 in this basis set.
[b]XXMO stands for the highest occupied molecule orbital (HOMO) of the anion or the lowest unoccupied molecular orbital (LUMO) of the neutral molecule.

tion interaction method with singles and doubles (MR-CISD) corrected partially for size-extensivity, namely, multireference averaged-quadratic coupled-cluster (MR-AQCC)[24] as implemented in the COLUMBUS[25] suite of programs. This method provides accuracy similar to the averaged coupled-pair functional (ACPF) method, but can be successfully used with a much smaller active space.[24] The active space consists of six electrons (seven for N_2^-) in six orbitals (seven for N_2^-) and the $3\sigma_g$ and $1\pi_u$ molecular orbitals (MOs) and the $2\pi_g$ and $4\sigma_u$ MOs were selected as valence holes and valence particles for N_2, respectively. The occupied σ_g MO was added into the active space of the anion.

The large atomic natural orbital basis of Widmark–Malmqvist–Roos[26] (WMR) described as $(14s9p4d3f/7s7p4d3f)$ was used in calculations of the N_2 and bound portion of N_2^- PECs. In order to allow the simulation of an extra electron autodetachment from N_2^-, the basis was augmented by diffuse sp-shells[27] located at the middle point of bonds. Adding a diffuse set practically does not influence the total energies of the bound states but allows the extra electron to move into the most diffuse MO of the ''anion'' (which corresponds in such a case to decay into the neutral system and a free electron) if the neutral parent cannot sustain the extra electron.

III. RESULTS AND DISCUSSION

Let us consider first the results of our CCSD(T)/WMR calculations for the ground state of N_2. Our computed bond length and vibrational frequency, 1.0984 Å and 2356.1 cm^{-1}, respectively, are in nice agreement with experimental 1.0977 Å and 2358.6 cm^{-1},[28] correspondingly. Since the CCSD(T) method is size extensive, the dissociation energy (D_e) of N_2 ($X\ ^1\Sigma_g^+$), calculated either as the difference in the total energies of the ground-state molecule and two isolated nitrogen atoms, or as the difference in the total energies at the equilibrium bond length and at $R(N–N) = 30$ a.u. (the state is $^7\Sigma_u^+$), is 9.67 eV and is close to the MRCI results[9,10] obtained with the bases of comparable quality. The $^2\Pi_g$ state of N_2^- is unstable by ≈ 2.0 eV with respect to the ground state of N_2; therefore, an extra electron cannot be attached in order to form a thermodynamically stable anion state.

Since the N_2^- ($^2\Pi_g$) state is unbound in the vicinity of its WMR equilibrium bond length, let us consider the decay of this state to the neutral ground state plus a free electron as a function of the exponent of an spd-shell added to the WMR basis set and placed at the middle of the $R(N–N)$ distance. The results of optimizations with the extended bases are presented in Table I, from where one can see a fast convergence of the total energy and bond length of N_2^- to those of the neutral molecule upon decreasing the exponent. With the exponent of 0.000 05, the results for the anion practically match the results obtained for the neutral parent.

Figure 1 presents the PESs of N_2 ($X\ ^1\Sigma_g^+$) and N_2^- ($^2\Pi_g$) obtained at the CCSD(T) level of theory with the WMR basis extended by seven diffuse sp-shells[27] with the use of an unrestricted HF reference function. As is seen, the total energy of N_2^- is below that of N_2 at the bond lengths from ≈ 1.4 to ≈ 2.5 Å. In order to confirm the existence of the temporary $^2\Pi_g$ state of N_2^-, we performed multireference highly correlated MR-AQCC calculations with the WMR basis at $R(N–N) = 1.7$ and 1.9 Å, where N_2^- was found to be bound at the CCSD(T)/WMR level. As shown by the entries of Table II, the N_2^- anion is below the energy of N_2.

The very existence of temporary N_2^-, which is electronically bound at the bond lengths from ≈ 1.4 to ≈ 2.5 Å, has to be due to the polarization of two nitrogen atoms of the neutral N_2 molecule by an extra electron in the opposite direction when the molecule is sufficiently excited to have the

TABLE II. Results of the calculations with the WMR basis for the neutral (N_2, $X\ ^1\Sigma_g^+$) and anion (N_2^-, $^2\Pi_g$) ground states at two internuclear separations of 1.7 and 1.9 Å. Total energies are in hartree, differences between the total energies (ΔE) are in eV.

Level	$R(N–N) = 1.7$ Å			$R(N–N) = 1.9$ Å		
	N_2	N_2^-	ΔE	N_2	N_2^-	ΔE
MR-SCF	−108.618 160	−108.702 613	2.298	−108.481 845	−108.600 471	3.227
MR-AQCC	−109.237 938	−109.247 264	0.247	−108.600 471	−109.149 212	1.240

large amplitude of nuclear motions. At smaller and larger bond lengths, this state decays to the ground or vibrationally excited states of the neutral N_2 molecules plus a free electron.

In conclusion, we would like to underline a unique character of the N_2^- anion: it does not exist at short bond lengths because the neutral N_2 molecule is not able to form a thermodynamically stable state. On the other hand, it does not exist at large bond lengths as well because the nitrogen atom has no positive electron affinity.

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[1] G. J. Schulz, Rev. Mod. Phys. **45**, 423 (1973).

[2] *Resonances*, edited by D. G. Truhlar (American Chemical Society, Washington, D.C., 1984).

[3] C. A. Weatherford and A. Temkin, Phys. Rev. A **49**, 2580 (1994).

[4] W. Sun, M. A. Morrison, W. A. Isaacs, W. K. Trail, D. T. Alle, R. J. Gulley, M. J. Brennan, and S. J. Buckman, Phys. Rev. A **52**, 1229 (1995).

[5] P. J. Rous, Surf. Sci. **326**, 67 (1995).

[6] R. Rumble, Jr., W. J. Stevens, and D. G. Truhlar, J. Phys. B **17**, 3151 (1984).

[7] C. A. Weatherford, F. B. Brown, and A. Temkin, Phys. Rev. A **35**, 4561 (1987).

[8] J. Almlöf, B. J. DeLeeuw, P. R. Taylor, C. W. Bauschlicher, Jr., and P. Siegbahn, Int. J. Quantum Chem., Symp. **23**, 345 (1989).

[9] H.-J. Werner and P. J. Knowles, J. Chem. Phys. **94**, 1264 (1991).

[10] R. S. Grev and H. F. Schaefer, III, J. Chem. Phys. **96**, 6850 (1992).

[11] R. J. Bartlett and J. F. Stanton, *Reviews in Computational Chemistry*, edited by K. B. Lipkowitz and D. B. Boyd (VCH, New York, 1994), Vol. 5, pp. 95-165.

[12] B. I. Schneider, M. Le Dourneuf, and V. K. Lan, Phys. Rev. Lett. **43**, 1926 (1979).

[13] A. U. Hazi, T. N. Rescigno, and M. Kurilla, Phys. Rev. A **23**, 1089 (1981).

[14] P. G. Burke, C. J. Noble, and S. Salvini, J. Phys. B **16**, L113 (1983).

[15] B. M. Nestmann and S. D. Peyerimhoff, J. Phys. B **18**, 4309 (1985).

[16] F. A. Gianrurco and F. Scheider, J. Phys. B **29**, 1175 (1996).

[17] G. L. Gutsev and L. Adamowicz, J. Chem. Phys. **102**, 9309 (1995).

[18] C. W. McCurdy and R. C. Mowrey, Phys. Rev. A **25**, 2529 (1982).

[19] M. Krauss and W. J. Stevens, J. Chem. Phys. **74**, 570 (1981).

[20] ACES II is a program product of the Quantum Theory Project, University of Florida, J. F. Stanton, J. Gauss, J. D. Watts, M. Nooijen, N. Oliphant, S. A. Perera, P. G. Szalay, W. J. Lauderdale, S. R. Gwaltney, S. Beck, A. Balkova, D. E. Bernholdt, K.-K. Baeck, P. Rozyczko, H. Sekino, C. Huber, and R. J. Bartlett. Integral packages included are VMOL (J. Almlöf and P. R. Taylor), VPROPS (P. R. Taylor), and ABACUS (H. J. Helgaker, Aa. Jensen, P. Jørgensen, and P. R. Taylor).

[21] G. D. Purvis, III, and R. J. Bartlett, J. Chem. Phys. **76**, 1910 (1982).

[22] M. Urban, J. Noga, S. J. Cole, and R. J. Bartlett, J. Chem. Phys. **83**, 4041 (1985).

[23] R. J. Bartlett, J. D. Watts, S. A. Kucharski, and J. Noga, Chem. Phys. Lett. **165**, 513 (1990).

[24] P. G. Szalay and R. J. Bartlett, Chem. Phys. Lett. **214**, 481 (1993).

[25] P. Shepard, I. Shavitt, R. M. Pitzer, D. C. Comeau, M. Pepper, H. Lishka, P. G. Szalay, R. Ahlrichs, F. B. Brown, and J.-G. Zhao, Int. J. Quantum Chem. **S22**, 149 (1988).

[26] P. O. Widmark, P. A. Malmqvist, and B. O. Roos, Theor. Chim. Acta **77**, 291 (1990).

[27] G. L. Gutsev and R. J. Bartlett, J. Chem. Phys. **105**, 8785 (1996).

[28] K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).