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METASTABILITY OF THE ^1D STATE OF THE NITROGEN NEGATIVE ION*

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Energies of the ^3P and ^1D states of N^- have been calculated using a first-order wave function designed to include the strongly structure-dependent part of the correlation energy. Comparing the N^- calculations to those of other appropriate systems, the remaining correlation energy is reliably estimated and the ^1D N^- state is predicted to be metastable, lying 0.844 eV below the ^2D state of N. Instability of the ^3P N^- state is predicted.

Several experiments[1] have indicated the existence of one or more states of the ion N^-. However, as the lowest state of atomic nitrogen lies below most estimates of the energy of a hypothetical ^3P ground state of N^-, the indicated N^- state(s) may be metastable with respect to electron detachment.[2] A ^3P state of N^- could be expected to decay rapidly into a free electron plus the ground ^4S state of N. Bates and Moiseiwitsch[3] have suggested that a ^1D state of N^- might be stable relative to all excited states of N, and would have a long lifetime because the process

$$N^-(^1D) \rightarrow N(^4S) + e$$

is forbidden. This Letter reports calculations comparing the energies of ^1D N^- and the first excited state (^2D) of atomic nitrogen.

Our calculations are based on wave functions designed to include in a nonrelativistic formulation the Hartree-Fock energy plus that part of the correlation energy which depends strongly upon the symmetry and shell structure of the electronic configuration. Such wave functions will then be subject to errors resulting from the omission of the remainder of the correlation energy and from relativistic effects. These residual errors, which vary smoothly with respect to the nuclear charge and number of electrons in an atomic system, can be closely estimated by interpolative methods.[4] This type of partitioning of the correlation energy was suggested by Silverstone and Sinanoğlu,[5] and we call the structure-sensitive part of the correlation energy the orbital correlation energy.

To calculate the orbital correlation energy we use what we call the first-order wave function, defined to be a configuration-interaction L-S eigenfunction including all orbital occupancies in which at most one electron is assigned to an orbital beyond the valence shell. For first-row atoms, this means configurations in which all, or all but one, of the electrons are assigned to Hartree-Fock $1s$, $2s$, or $2p$ orbitals. The orbital correlation energy is the difference between the energy of the first-order wave function and the Hartree-Fock energy.

Table I. Energies, in Hartree units, of first-order wave functions. These calculations are believed to be within 0.0001 Hartree unit of the exact first-order energy.

State and atom	No. configurations	Energy	Orbital correlation energy
^2D N	195	−54.35547	−0.05932
^1D N^-	105	−54.30922	−0.04235
^2D O^+	195	−74.29811	−0.06481
^1D O	105	−74.77831	−0.04910

Our first-order wave function includes configurations of the types suggested for the same purpose by Silverstone and Sinanoğlu, with the difference that their configurations refer to Slater determinants while ours refer to L-S eigenfunctions. Our first-order wave function includes determinants which are not included in the Silverstone-Sinanoğlu enumeration, but whose existence depends upon the electronic shell structure. The significance of this difference is indicated by recent work of Sinanoğlu and Öksüz,[6] who find a structure-dependent correlation energy of −1.31 eV for ^2D N, while our first-order wave function yields an orbital correlation energy of −1.61 eV.

Using first-order wave functions with basis sets sufficiently large to give convergence in energy to within 0.0001 Hartree unit, we have calculated the energies of the lowest ^2D state of N and the lowest ^1D state of N^-. To aid in estimation of the residual errors, we also carried out corresponding calculations on O^+ (^2D) and O (^1D), and on the ground states of C, C^-, N^+, N, N^-, O^+, O, O^-, F^+, F, F^-, and Ne^+. Some of these calculations are described in Table I.

The calculated energies were processed by taking differences corresponding to electron affinities of the neutral atoms and positive ions. Following this, the computed electron affinities of positive ions were compared with the experimental ionization potentials.[7] It was found that the residual error in the electron affinities indeed varied regularly, depending mainly on the number of electrons, and that a rather good estimate of the electron affinity of a neutral atom could be obtained by assuming the calculated value to have the same residual error as was found for the electron affinity of the isoelectronic positive ion. Affinities estimated on the basis of this simple assumption are shown in Table II.

Table II. Estimated and measured values of the electron affinities of neutral atoms, in eV.

	Estimated from isoelectronic positive ion	Final estimate	Experiment
^3P C	1.112	1.242	1.25 ± 0.03[a]
^4S N	−0.408	−0.213	...
^2D N	0.649	0.844	...
^3P O	1.201	1.461	1.465 ± 0.005[b]
^2P F	3.128	3.453	3.448 ± 0.005[c]

[a] M. Seman and L. M. Branscomb, Phys. Rev. 125, 1602 (1962).

[b] L. M. Branscomb, D. S. Burch, S. J. Smith, and S. Geltman, Phys. Rev. 111, 504 (1958).

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Better estimates of the electron affinities of neutral atoms can be produced by noting that the results just cited deviate from experimental values by amounts approximately proportional to the number of $2p$ electrons in the neutral atom. There is some theoretical justification for such behavior, as more extensive ab initio calculations[8] on B and B^- have shown that higher order correlations within the $1s^22s^2$ core contribute relatively little to the electron affinity of boron. Assuming, then, an additional residual error of 0.065 eV per $2p$ electron, we obtain the final estimates listed in Table II.

For all three atoms whose electron affinities are known, these final estimates agree with the experimental data to within the claimed accuracy of measurement, and we are led to conclude that the estimates for the unmeasured affinities of N(^4S) and N(^2D) are of comparable reliability. We therefore predict the instability of the hypothetical ^3P state of N^-, and the existence of a metastable ^1D state of N^- lying 1.539 eV above the ^4S ground state of N and 0.844 eV below the ^2D N excited state.

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LIGHT SCATTERING FROM ELECTRON PLASMAS IN A MAGNETIC FIELD

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We have observed Raman scattering from the hybrid plasma mode in n-GaAs and its coupling with the Bernstein modes at harmonics of the cyclotron frequency.

We report Raman scattering of 1.06-μ radiation by two coupled elementary excitations of the electron gas in GaAs, the hybrid plasma mode and the collective Bernstein modes at $n\omega_c$ with $n \geqslant 2$ (where $\omega_c = eB/m^*c$ is the cyclotron frequency). Raman scattering by various modes of electron gas in semiconductors, including pure plasmons,[1,2] pure collective Bernstein modes,[2-4] single-particle excitations of the Landau levels of the electron gas,[2,3] and the coupled optic-phonon-plasmon modes,[1,5] has been recently reported. In the present experiments the application of a magnetic field to an electron gas gives rise to observable Raman scattering from the hybrid plasma mode[6] which involves the coupling between the plasmons and ω_c, the cyclotron-frequency excitations. In addition, scattering in the region of $\omega_p = (n^2-1)^{1/2}\omega_c$, where $\omega_p = (4\pi ne^2/m^*\epsilon_0)^{1/2}$ is the plasma frequency of the electron gas, is expected[7] to give information about the coupling between the Bernstein modes[8] and the hybrid mode. The frequency shifts and the line broadening of the scattered light in our experiments show the effect of such coupling.

The scattering experiments were carried out at 1.06 μ using a 3- to 10-W Nd-doped yttrium-aluminum-garnet laser. GaAs with electron concentrations from 1.6×10^{16} cm^{-3} to 1.4×10^{17} cm^{-3} were investigated. The laser was incident along a $\langle100\rangle$ axis and the scattered radiation was collected along a $\langle010\rangle$ axis. A superconducting solenoid provided magnetic fields up to 100 kOe. Two scattering geometries were investigated: $\vec{k}\perp\vec{B}$ (Fig. 1) and $\vec{k}$ at 45° to $\vec{B}$ (Fig. 2), where $\vec{k} = \vec{k}_i - \vec{k}_s$ is the wave vector of the excitation causing the scattering and $\vec{k}_{i,s}$ are the wave vectors of the incident and the scattered radiation, respectively. The experiments were carried out at a sample temperature of 300°K where the electron gas is nondegenerate. The scattered light was analyzed with a tandem spectrometer and detected with a cooled S-1 phototube.

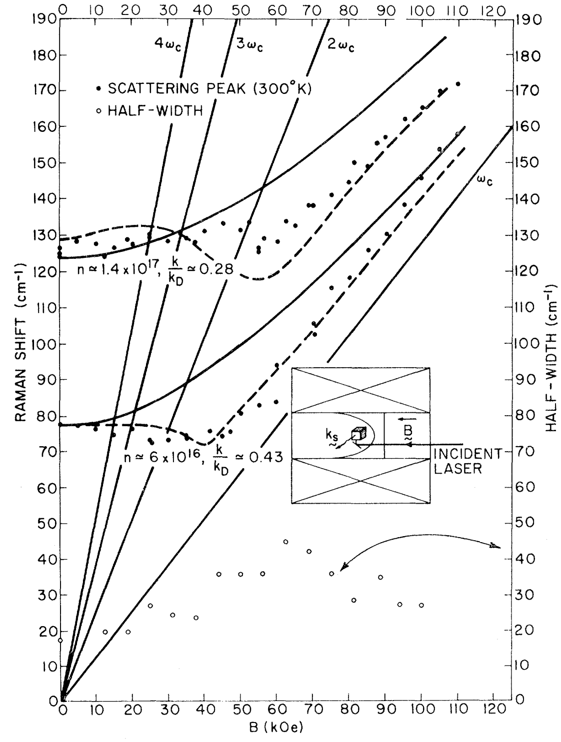

FIG. 1. Frequency shift as a function of $\vec{B}$ of inelastically scattered light with $\vec{k}\perp\vec{B}$ from coupled plasmon–cyclotron modes of electron gas in n-GaAs for three different electron densities, and half-width of the above scattered light for $n_e \approx 1.6\times10^{17}$ n-GaAs sample.