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Ionization Potential of Ammonia—Some Implications concerning Koopman's Theorem

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THE ground state of the NH_3^+ ion has been studied by the SCF LCAO method, using Hartree-Fock AO. The values of the atomic integrals have been taken from a previous work on the neutral NH_3 molecule.[1] The calculations have been performed both for the pyramidal and the planar configuration. The ionization potential has been calculated by Koopman's theorem as well as by taking the difference between the energy of the molecule and the ion. The former is designated by $\mathcal{E}$, the latter by ΔE, and the experimental value[2] by I. The results are given in Table I.

Contrary to Mulliken's[3] suggestion, the direct calculation gives a better value for the ionization potential than that obtained from the theorem of Koopman. It is assumed in this theorem that the orbitals of the ion are the same as those of the molecule. When one calculates the self-consistent orbitals for the ion, the energy necessarily comes out to be lower than that obtained when the self-consistent orbitals of the molecule are used for the ion. Thus ΔE is less than $\mathcal{E}$.

If Koopman's theorem gives an ionization potential which is too high, ΔE probably is closer to the experimental value than $\mathcal{E}$. If, on the contrary, $\mathcal{E}$ is too small, it represents the ionization potential better than ΔE.

Table I. Computed ionization potentials of NH_3. The experimental value for the planar case is not known, as the molecule is a fictitious one, but it should not greatly differ from 10.15 ev.

	Pyramidal case	Planar case
$\mathcal{E}$	14.0 ev	12.6 ev
ΔE	12.1 ev	10.5 ev
I	10.15 ev	···

Existing data are summarized in Table II.[4–13] It is to be noticed that in all cases known, $\mathcal{E}$ is less than I when the MO are expressed by Slater AO with Slater's exponents, while the reverse is true when they are expressed by Hartree-Fock AO. In the latter case, an independent calculation of the energy of the ion might give a better value only if a Hartree-Fock basis is used.

A complete account on the work on NH_3^+ will be published elsewhere.

Table II. Ionization potentials calculated by Koopman's theorem.

Molecule	Reference	Type of AO	$\mathcal{E}$	I
CH	4	Slater	11.1	11.13
OH	4	Slater	10.8	13.2
FH	4	Slater	12.6	15.8
N_2	5	Slater	14.8	15.6
O_2	6	Slater	11.0	12.2
CO	7	Slater	13.7	14.0
NO	8	Slater	9.1	9.2
F_2	9	Slater	14.3	16.5
H_2O	10	Slater	11.8	12.6
NH_3	11	Slater	9.9	10.2
OH	12	HF	16.2	13.2
FH	13	HF	17.3	15.8
NH_3	1	HF	14.0	10.2

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