This function depends on the electronic coordinates $\mathbf{u}_i$ and parametrically on the nuclear conformation, which may be specified by a set of internuclear distances R_i and angular coordinates θ_k,

$$\Psi = \Psi(\mathbf{u}_i;\, R_j,\, \theta_k).$$

We now introduce a scale factor α,

$$\Phi_\alpha(\mathbf{u}_i,\, R_j,\, \theta_k) = \alpha^{(3N/2)}\Psi(\alpha\mathbf{u}_i,\, \alpha R_j,\, \theta_k)$$

(N is the number of electrons),

$$W(\alpha) = \alpha^2 T(\alpha R_j,\, \theta_k) + \alpha V(\alpha R_j;\, \theta_k),$$

$$(dW/d\alpha) = 2\alpha T(\alpha R_j,\, \theta_k) + V(\alpha R_j,\, \theta_k)$$
$$+ \alpha^2 \sum_i R_i[\partial T(\alpha R_j,\, \theta_k)/\partial R_i]$$
$$+ \alpha \sum_i R_i[\partial V(\alpha R_j,\, \theta_k)/\partial R_i]. \quad (1')$$

Since we assumed that we had the exact wavefunction for $\alpha=1$, $(dW/d\alpha)_{\alpha=1}=0$ and we get the required formula

$$2T + V + \sum_i R_i(\partial W/\partial R_i) = 0. \quad (2)$$

Here the sum may run over any set of internuclear distances, which together with angular coordinates is sufficient to specify the structure (for instance all bond lengths). Equation (1) is thus a special case of Eq. (2).

The important point of the proof is that angular coordinates are unchanged by scaling and therefore give no contribution to the sum. As a consequence we may use a set of independent internuclear distances in Eq. (2) while in Eq. (1) we were forced to use *all* internuclear distances and they are independent only for molecules having two or three atoms.

From the form of (2) we see that for every set of angles for which the equations $(\partial W/\partial R_i)=0$ (all R_i) have solutions $R_i^0(\theta)$, the virial theorem holds in its simple form

$$W(R_i^0, \theta) = -T(R_i^0, \theta) = 2V(R_i^0, \theta). \quad (3)$$

We may discuss the energy change with changes in an angular coordinate as a change in electronic, kinetic, or potential energy, if we see to it that for all values of the angle we keep the bond distances at their corresponding equilibrium values.

Equation (2) and its derivatives, with respect to different internal coordinates, may be used to obtain derivatives of the total electronic, kinetic, and potential energies, with respect to internal coordinates, at the equilibrium nuclear conformation from experimental force constants (harmonic and higher).

This may, for instance, facilitate the generalization to polyatomic molecules of the electronic model used by Parr and Borkman[3] to describe the vibration spectra of diatomic molecules.

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Application of Ion Cyclotron Resonance to the Study of Inelastic Excitation by Low-Energy Electrons*

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The geometry of the resonance cell employed for ion cyclotron resonance spectroscopy[1-3] is ideally suited for studying inelastic excitation by low-energy electrons. It has been shown that the electron beam traverses a parabolic potential well between the trapping electrodes, the depth of which is approximately half the applied trapping voltage.[3,4] Low-energy electrons generated by impact excitation of an atomic or molecular energy level can be trapped in the resonance cell if their final translational energy is insufficient to escape the preset depth of the potential well. These electrons can be drifted from the source to the resonance region by applying the usual static drift field E normal to the primary magnetic field H.[4] The electron drift velocity in this crossed field geometry, given by cE/H, is independent of *both* charge and mass. For typical values of E and H the drift velocity is in the range of 10^1–10^3 cm/sec. In the lower range of accessible drift velocities, the residence time of electrons in the resonance cell approaches 0.1 sec.

The cyclotron resonance frequency of an electron is too high (1–10 GHz for reasonable magnetic field strengths) to observe electron cyclotron resonance with the marginal oscillator–detector. The dissociative attachment process,

$$e + CCl_4 \rightarrow Cl^- + CCl_3, \quad (1')$$

has recently been shown to proceed with a large cross section (160 Å²) for zero-energy electrons.[5,6] This, combined with the long residence time of trapped electrons in the apparatus, allows for conversion of low-energy electrons to Cl^-, which is readily observed with the marginal oscillator–detector. Difficulties due to the several electron-impact processes known to generate Cl^- from CCl_4 above ~0.2-eV electron energy[5,6] are obviated by the trapping of only low-energy electrons and their detection with a minimal scavenger concentration.

As an example of this application of ion cyclotron resonance spectroscopy, an excitation spectrum of N_2 at 2×10^{-5} torr containing 0.1% CCl_4 has been recorded (Fig. 1) by monitoring the Cl^- produced as a function of electron energy. The emission current was regulated at 10^{-8} A to avoid space-charge broadening of the electron energy distribution, the width of which is estimated to be 0.2 eV. The spectrum in Fig. 1 reveals several well-resolved excitation peaks, the positions[7] and intensities of which are in excellent agreement with previous studies of threshold electron-impact excitation of N_2.[8-11]
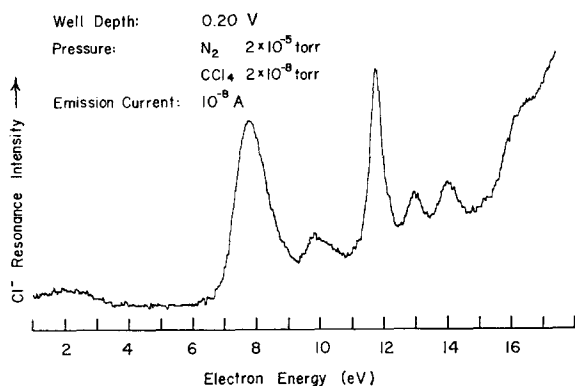

Well Depth: 0.20 V
Pressure: N_2 2×10^{-5} torr
    CCl_4 2×10^{-8} torr
Emission Current: 10^{-8} A

Electron Energy (eV)

FIG. 1. Inelastic excitation spectrum of N_2 obtained by scavenging trapped low-energy electrons with CCl_4 and measuring the resultant Cl^- with ion cyclotron resonance spectroscopy. The prominent features at 7.8 and 11.8 eV correspond, respectively, to excitation of the $B\ {}^3\Pi_g$ and $E\ {}^3\Sigma_g^+$ states of N_2. The peak at 2.0 eV results from temporary negative ion formation.

Brongersma and Oosterhoff[9] have recently improved the resolution and sensitivity of the original trapped electron experiments by Schulz[8] by incorporating a retarding potential difference (RPD) source of quasi-monoenergetic electrons in a redesigned apparatus. They provide convincing evidence for assignment of the prominent peaks at 7.8 and 11.8 eV to excitation of the $B\ {}^3\Pi_g$ and $E\ {}^3\Sigma_g^+$ states of N_2, respectively.

While Brongersma and Oosterhoff measured the trapped electron currents directly, other investigators[10-12] have employed SF_6 as a scavenger for low-energy electrons, detecting the resultant SF_6^- using standard mass-spectrometric methods.[13] Brongersma[9b] has noted that in certain instances (notably benzene) the electron scavenging method yields peak intensities in significant disagreement with intensities derived from the directly measured electron current. In all cases examined to date, including benzene, the ion cyclotron resonance method has been found to corroborate the trapped electron peak intensities.

No modifications of the standard ion cyclotron resonance instrumentation are required to obtain inelastic excitation spectra by the method described. The resolution, at present limited by the 0.2-eV width of the electron energy distribution, could be considerably improved by incorporation of an RPD source of quasimonoenergetic electrons. A perusal of available high-resolution trapped electron spectra makes clear that such enterprise has little advantage except in the case of diatomic molecules, where vibrational fine structure is occasionally resolved.[9]

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Change of High-Frequency Permittivity at an Orientational Order–Disorder Transformation: A Method of Detecting Very Slow Transformations*

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Ice III, which is orientationally disordered, transforms gradually to the orientationally ordered ice IX on cooling below about $-100°C$.[1] The orientation polarization of ice III was followed[1] throughout the dispersion region over the whole course of the transformation, and in particular the limiting high-frequency permittivity ϵ_∞ was measured. It changed gradually through the transition, and the values for ice III and IX extrapolated somewhat arbitrarily to $-100°C$ are 3.96 and 3.74, respectively, which differ by 5.7%.