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Observability of Rearrangement Energies and Relaxation Times*

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We present a clarification of the often misunderstood concept of rearrangement that affects particle removal from finite fermion systems. A separation energy is defined which depends on the speed of removal as a result of physical rearrangement processes. It is shown how single-particle eigenvalues can be observed when a single-particle description applies to the many-body system. Calculations of atomic rearrangement energies are discussed, and a linear Z dependence is derived. The photo-ionization spectrum for 1s electrons from Ne is used as a quantitative example to extract rearrangement energy and time. Possible application to nucleon-removal data analysis is discussed.

I. INTRODUCTION

Extensive theoretical and experimental effort has been expended to calculate and measure single-particle binding energies in many-body systems. If a particle is removed, it is evident that the remaining particles are affected and will generally respond with some sort of rearrangement. This rearrangement contributes to the energy needed to remove a particle and must be considered in comparisons between experiment and theory. However, the observability of rearrangement is not a well-accepted fact. Model-dependent unobservable quantities have been defined as rearrangement energy. In this paper we will discuss quantities that are related to physical rearrangement processes and describe how to observe them, i.e., how eigenvalues can be measured and compared with calculations.

Physical intuition suggests that if a particle is removed suddenly (vanishes instantly) or, on the other hand, adiabatically (is dragged out very slowly), the remaining particles will respond differently. This is the basis for the concept of a relaxation or rearrangement time of the system—the time required for a collective response to the removal. In a sudden removal the system will be shattered. In quantum-mechanical terms, other particles are "shaken"[1] into the continuum or previously unoccupied bound states. There is no time to rearrange. It was suggested that a "frozen orbit"[2,3] picture applies in this limit. In the other limit, the particle is dragged out and the remaining system adjusts at each stage. Shaking can be made arbitrarily small.

Let us introduce specific definitions for the example of the 1s-electron photo-ionization of a Ne atom (details will be discussed in Secs. III and IV). The rearrangement energy Δ_{1s} is defined here as the distance of the centroid $s_{1s}(\tau)$ for the spectrum of states with one hole at the 1s level to the position $s_{1s}(\infty)$ of the peak with the lowest missing energy, i.e., $\Delta_h(\tau) \equiv s_h(\tau) - s_h(\infty)$. The variable τ denotes a removal time constant. One can calculate the quantity $s_h(\infty)$ as the total energy of the Ne ion with one hole at the hth level minus that of the Ne atom. The Hartree-Fock (HF) approximation is good enough in this specific case to compute $s_h(\infty)$ as well as $s_h(0)$ to an accuracy of about 1 eV; $-s_h(0)$ is simply ϵ_h, the 1s-electron eigenvalue in Ne. In other words, $s_h(\infty)$ is the separation energy for "coldest" or perfectly adiabatic removal where the system is allowed to fully rearrange or relax; $s_h(\infty)$ is a removal threshold. In atoms, the rearrangement energy Δ_h has also been called the "cloud adaption process" energy.

In order to determine the rearrangement energy $\Delta_h(\tau)$ from a given particle-removal spectrum which starts with a peak at $s_h(\infty)$, one has to know the degree to which the removal is not adiabatic (cf. Sec. III). The position $s_h(\infty)$ of the leading peak is practically independent of the speed of removal. The observed agreement of "relaxed" or adiabatic total energy difference calculations with the leading photo-ionization peaks has led to the erroneous view that removals of strongly bound electrons are essentially adiabatic.[2,3] The relevant spectra clearly exhibit nonadiabatic, i.e., shaking effects which have recently been correctly identified.[4] However, the present literature about HF calculations still contains various confusing notions on the relation of HF eigenvalue spectra, photo-ionization spectra, and removal energies. We, therefore, attempt a clarification by reviewing the theoretical significance of the methods used in calculating separation energies.

In Sec. II, we consider the first-order deviations from the adiabatic and sudden limits in particle removal. Section III describes the relation of observed spectra, spectroscopic factors, and rearrangement energies. As an illustrative example, the photo-ionization removal of 1s electrons from Ne is analyzed in detail in Sec. IV. The general relationship of HF calculations and rearrangement is discussed in Sec. V. We also show that the rearrangement energy for the removal of inner electrons (and for β decay) is a linear function of nuclear charge, in contrast to previous results in the literature.[5,6] Section VI contains our conclusions and suggestions.

II. SUDDEN AND ADIABATIC LIMITS

Consider a Hamiltonian which changes by a finite, fixed amount H' during a time interval τ:

$$H'(\tau)=H(\tau)-H(0)=\tau\langle\partial H/\partial t\rangle=\tau\langle\partial H/\partial a\rangle\langle\dot{a}\rangle\ . \qquad (2.1)$$

The average is over the "switch-on" interval τ and $\dot{a}$ is the rate of change of the Hamiltonian which is time dependent through a time-dependent parameter $a(t)$, with $a(0)\equiv 0$ and $a(\tau)\equiv 1$. A typical example would be $a=1-n_h$, where n_h is the occupation probability for the hth (HF) orbital. We are interested in the limits $\tau\to 0$ and $\to\infty$ for fixed H'. Let

$$H(a)u_n(a)=u_n(a)E_n(a) \qquad (2.2)$$

and write the total time-dependent wave function

$$\Psi(t)=\sum\nolimits_n c_n(t)u_n(0)e^{-iE_n(0)t/\hbar}\ . \qquad (2.3)$$

Inserting this into the Schrödinger equation $i\hbar\dot{\Psi}=H\Psi$, we get, after the usual[1,7] multiplication with $\int d\vec{q}\,u_m^* e^{iE_m(0)t/\hbar}$,

$$i\hbar\dot{c}_m(t)=\sum\nolimits_n c_n(t)e^{i[E_m(0)-E_n(0)]t/\hbar}H'_{mn}(t)\ , \qquad (2.4)$$

with

$$H'_{mn}(a(t))=\int d\vec{q}\,u_m^*(0)H'(a)u_n(0)\ . \qquad (2.5)$$

We denote the initial state by 1, i.e., $c_n(0)=\delta_{n1}$. For sufficiently weak relative changes (perturbations) in the Hamiltonian, we can start an iterative solution by setting $c_n(t)\approx\delta_{n1}$ on the right-hand side of Eq. (2.4) for $m\neq 1$ and integrating:

$$c_m(\tau)=-\frac{1}{\hbar}\int_0^\tau dt\,e^{i[E_m(0)-E_1(0)]t/\hbar}H'_{m1}(t) \qquad (2.6\text{a})$$

$$=-\frac{e^{i[E_m(0)-E_1(0)]\tau/\hbar}}{E_m(0)-E_1(0)}H'_{m1}(\tau)$$

$$+\int_0^\tau dt\,\frac{e^{i[E_m(0)-E_1(0)]t/\hbar}}{E_m(0)-E_1(0)}\frac{\partial}{\partial t}H'_{m1}\ . \qquad (2.6\text{b})$$

We restrict ourselves to such changes in the Hamiltonian where $\partial H'_{m1}/\partial t$ does not vary rapidly in a time interval that is small compared to τ. That is, we consider an essentially trapezoidal $H'_{m1}(t)$ from 0 to τ, so that $\partial H'_{m1}/\partial t$ has a width of order τ. Then the integral term in Eq. (2.6b) can be made arbitrarily small if τ is sufficiently large as compared to $\hbar/[E_m(0)-E_1(0)]$. Therefore, in the *adiabatic* limit,

$$\tau\gtrsim\frac{1}{\dot{a}_{\max}}\gg\frac{\hbar}{E_m(0)-E_1(0)}\ , \qquad (2.7)$$

$$|c_{m\neq 1}(\tau)|^2\approx\frac{|H'_{m1}(\tau)|^2}{[E_m(0)-E_1(0)]^2}=O(\dot{a}^2)\ . \qquad (2.8)$$

That is, the transition probability to any state $m\neq 1$, the amount of "shaking"[1] is given by a function proportional to the square of the rate of change in the Hamiltonian. Hence, shaking vanishes for $\dot{a}_{\max}\to 0$ or $\tau\to\infty$ and fixed H'. Note that the dependence on speed, or the amount of shaking at a given low speed is proportional to both the square of the perturbation matrix elements and the level densities.

If the change occurs arbitrarily fast, $\tau\to 0$ for fixed H', we expand the wave function in terms of the eigensolutions of Eq. (2.2) for any time and obtain

$$-\frac{\hbar}{i}\frac{\partial}{\partial t}\sum_n c_n(t)u_n(a)=\sum_m c_m(t)u_m(a)E_m(a)\ ,$$
$$-\frac{\hbar}{i}\sum_n c_n(t)u_n(a)\Big|_0^\tau=\int_0^\tau dt\sum_m c_m(t)u_m(a)E_m(a)\ . \qquad (2.9)$$

Since $c_n(0)=\delta_{n1}$,

$$\sum_n c_n(\tau)u_n(1)=u_1(0)-\frac{i}{\hbar}\int_0^\tau dt\sum_m c_m(t)u_m(a)E_m(a)\ , \qquad (2.10)$$

and

$$c_n(\tau)=f_{n1}-\frac{i}{\hbar}\int_0^\tau dt\sum_m c_m(t)E_m(a(t))$$
$$\times\int d\vec{q}\,u_n^*(1)u_m(a(t))\ , \qquad (2.11)$$

where

$$f_{nm}\equiv\int d\vec{q}\,u_n^*(1)u_m(0)\ . \qquad (2.12)$$

Hence for $\tau\to 0$ we get for the transition probability to any configuration m

$$|c_m(\tau)|^2=|f_{m1}|^2\equiv S_{m1}\ , \qquad (2.13)$$

i.e., the "spectroscopic factors" S. The difference between this result and Eq. (2.8) must come from a contribution of the integral term in Eq. (2.6b). We, therefore, have a necessary condition for the *sudden* limit:

$$\tau\lesssim\frac{1}{\dot{a}_{\min}}\ll\frac{\hbar}{E_m(0)-E_1(0)}\ , \qquad (2.14)$$

where τ is the width of $\partial H'_{m1}/\partial t$. A comparison with the $\tau\to\infty$ limit, Eq. (2.7), shows that for all finite transition times, the probability of remaining in the initial configuration will be enhanced (relative to the sudden limit), whereas shakings, transitions to $m\neq 1$, are reduced relative to the value given by spectroscopic factors. This is readily seen in cases where one can set $\int d\vec{q}\,u_n^*(a(\tau))u_m(a(t))\approx\delta_{nm}$ in the time integral, which is then

$$\simeq \frac{i}{\hbar}\int_0^\tau dt\, c_n(t)\, E_n(a(t)) \simeq \frac{i}{\hbar}\,\tau\,\frac{c_n(0)\,E_n(0) - c_n(\tau)\,E_n(1)}{2}\ , \tag{2.15}$$

so that

$$c_n(\tau) \approx \frac{f_{n1} - (i/2\hbar)\tau E_n(0)\delta_{n1}}{1 + (i/2\hbar)\tau E_n(1)}\ . \tag{2.16}$$

For finite shaking where $|f_{11}| < 1$, we get $|c_1| > |f_{11}|$ (whereas no change occurs for $f_{11} = 1$) and $|c_{n\neq1}| < |f_{n1}|$ to first order in τ.

III. OBSERVABILITY OF REARRANGEMENT

The spectroscopic factors defined in Eqs. (2.12) and (2.13) can be determined by an analysis of the photo-ionization spectrum. In this section, we will show that the spectroscopic factors are also related to the rearrangement energy and the single-particle eigenvalue so that these quantities can indeed be observed under certain conditions.

Consider a photo-ionization experiment using hard x rays. In this case, the photoelectron is removed very rapidly and final-state interactions between the outgoing electron and the residual ion can be neglected. Then the final state is given by

$$|\Psi_f\rangle = a_k^\dagger |N-1,\ \alpha\rangle\ , \tag{3.1}$$

where $|N-1,\ \alpha\rangle$ is the αth excited state of the $(N-1)$-electron system, and $a_k^\dagger$ creates an electron with energy ϵ_k. The number of transitions per second from an initial configuration of a photon plus an N-electron atom in its ground state $|N\rangle$ to the final state above is[8]

$$w = (2\pi/\hbar)\left|\langle N-1,\ \alpha|a_k \sum_{ij} V_{ij}^{\mathrm{em}} a_i^\dagger a_j |N\rangle\right|^2 \times \delta(\epsilon_k + E^\alpha(N-1) - \hbar\omega - E(N))\ , \tag{3.2}$$

where V^{em} is the electromagnetic interaction.

For hard x rays, the energy ϵ_k is large enough so that we can set $a_k|N\rangle = 0$. Of course, this is always the case in a pure single-particle approximation for the ground state. Then

where w_h, the transition probability for the removal of the electron with quantum numbers h, is given by

$$w_h = (2\pi/\hbar)|\langle N-1,\ \alpha_h|a_h|N\rangle|^2 |V_{kh}^{\mathrm{em}}|^2 \times \delta(\epsilon_k + E^{\alpha_h}(N-1) - \hbar\omega - E(N))\ . \tag{3.3}$$

The density of states represented by the δ function above can be included in the normalization of the states $|N-1,\ \alpha_h\rangle$. For fixed photon energy, w_h will display peaks as a function of ϵ_k corresponding to the discrete energies $E^{\alpha_h}(N-1)$. There will also be a continuous part of the spectrum beginning at the threshold for shake off of another electron. In the case of rapid removal, we expect the energy range of the ion states which contribute to w_h to be small compared to ϵ_k and, therefore, we ignore the dependence of V_{kh}^{em} on ϵ_k. Then the area under the curve of w_h as a function of ϵ_k is proportional to the spectroscopic factors $|\langle N-1,\ \alpha_h|a_h|N\rangle|^2$ introduced by Eqs. (2.12) and (2.13).

In actual experimental measurements, there will be other contributions to the spectrum (e.g., inelastic scattering of the outgoing electron) which disturb the extraction of the spectroscopic factors. These must be accounted for as shown in the analysis of the Ne photoelectron data in Sec. IV.

From the derivation above and the discussion of the sudden and adiabatic limits of time-dependent perturbation theory in Sec. II, we see that the spectroscopic factors are displayed only when the particle is removed with sufficiently high velocity. If the removal were completely adiabatic, only the lowest energy state in the group $|N-1,\ \alpha_h\rangle$ would be populated.

Let $\alpha_h = 0_h$ denote the $(N-1)$-electron state with one hole at the level h and no further excitation. Define the rearrangement energy $\Delta_h(\tau)$ as the difference of the single-hole state energy $E^{0_h}(N-1) - E(N)$, and the centroid

$$s_h(\tau) \equiv \sum_{\alpha_h} |c_{\alpha_h}(\tau)|^2 [E^{\alpha_h}(N-1) - E(N)]\ , \tag{3.4}$$

i.e.,

$$\Delta_h(\tau) \equiv s_h(\tau) - E^{0_h}(N-1) + E(N)\ . \tag{3.5}$$

In Eq. (3.4), the sum over α_h includes the state 0_h and implies integration over the continuous part of the spectrum.

In the sudden limit, $\tau = 0$, the rearrangement energy $\Delta_h(0)$ is given by the spectroscopic factors [see Eq. (2.13)], and peak energies, i.e., by the ionization curves. It is thus an observable.

We now show that this, in turn, can be related to the eigenvalues of a single-particle Hamiltonian. Consider

$$\begin{aligned}\langle N|a_h^\dagger H a_h|N\rangle &= \langle N|\{a_h^\dagger,\ H\}a_h - Ha_h^\dagger a_h|N\rangle \\ &= \langle N|\ -\sum_i t_{ih} a_i^\dagger a_h \\ &\quad - \tfrac{1}{2}\sum_{ijl}(v_{ijhl} - v_{ijlh}) a_i^\dagger a_j^\dagger a_l a_h|N\rangle \\ &\quad + \langle N|Ha_h^\dagger a_h|N\rangle\ ,\end{aligned} \tag{3.6}$$

where

$$H = \sum_{ij} t_{ij} a_i^\dagger a_j + \tfrac{1}{2}\sum_{ijkl} v_{ijlk} a_i^\dagger a_j^\dagger a_k a_l\ . \tag{3.7}$$

In the single-particle approximation where $|N\rangle$ is given by a determinant of orthonormal single-particle wave functions (see Sec. V), it is easy to show that

$$\langle N|a_h^\dagger H a_h|N\rangle = -\epsilon_h + E(N)\ , \tag{3.8}$$

where ϵ_h is the eigenvalue of H for the hth single-particle function of an orbital occupied in the N-particle ground state. Also,

$$\langle N|a_h^\dagger H a_h|N\rangle = \sum_{\alpha_h} |\langle N-1,\ \alpha_h|a_h|N\rangle|^2 E^{\alpha_h}(N-1)$$

$$= s_h(0) + E(N)\,, \qquad (3.9)$$

where $E^{\alpha_h}(N-1) = \langle N-1,\ \alpha_h|H|N-1,\ \alpha_h\rangle$. Therefore, comparing Eqs. (3.9) and (3.8) and using Eqs. (3.4) and (2.13),

$$\epsilon_h = E(N) - \Delta_h(0) - E^{0_h}(N-1) = -s_h(0)\ . \qquad (3.10)$$

Thus, when a single determinant is a good description of the ground state, the single-particle eigenvalues can be related to measurable quantities.

If one moves from the sudden to the adiabatic limit $\tau \rightarrow \infty$, the coefficients $c_{\alpha_h}(\tau) \rightarrow \delta_{\alpha,0}$ in Eq. (3.4) and the centroid moves from $-\epsilon_h$ to $E^{0_h}(N-1) - E(N)$. Thus, it is clear that $s_h(\infty)$ is a removal threshold, i.e., it is the separation energy for coldest or perfectly adiabatic removal. Also, Eq. (3.5) can be written

$$\Delta_h(\tau) = s_h(\tau) - s_h(\infty)\ , \qquad (3.11)$$

demonstrating how the rearrangement energy goes to zero in the adiabatic limit. For any finite removal time, the quantity $\Delta_h(\tau)$, as defined in Eq. (3.5), is the energy left due to incomplete rearrangement in the residual system with one hole in the hth level.

IV. ANALYSIS OF PHOTO-IONIZATION OF K ELECTRON FROM Ne

We illustrate the results of Sec. III by examining the photo-ionization spectrum for the removal of a 1s electron from the Ne atom. There are extensive data available in the literature for this experiment. Also, Ne has a relatively simple spectrum for which HF theory gives a good description. As discussed in Sec. V (see Fig. 2), relativistic and correlation effects for low Z are very small compared to rearrangement energies.

TABLE I. Main peak and shake-up states for the 1s photo-ionization spectrum of Ne from Ref. 4.

Line No.	Excitation energy	Relative intensity	State
0	870.2	0.74	$1s\ 2s^2\ 2p^6$
7	907.5	0.018	$1s\ 2s^2\ 2p^5\ 3p$
8	910.9	0.019	$1s\ 2s^2\ 2p^5\ 3p$
9	912.5	0.011	$1s\ 2s^2\ 2p^5\ 4p$
10	914.4	0.004	$1s\ 2s^2\ 2p^5\ 5p$
11	916.6	0.004	$1s\ 2s^2\ 2p^5\ 4p$
12	931.2	0.004	$1s\ 2s\ \ 2p^6\ 3s$

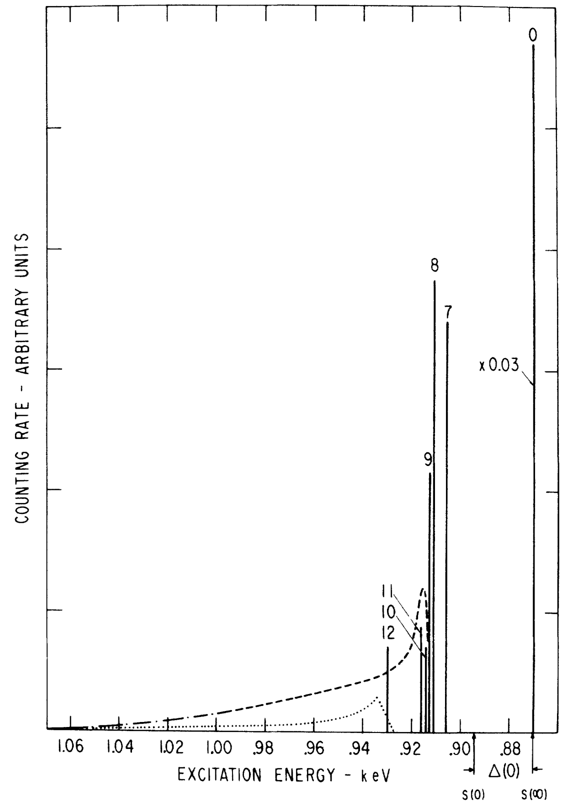

FIG. 1. Schematic representation of the Ne 1s photo-ionization spectrum. The main peak, denoted by 0, has a width of 0.8 eV and the shake-up peaks 7–12 have been given a width of 1.2 eV. The positions and strengths of these peaks are from Ref. 4. The dashed line represents shake off of one electron from Ref. 10. The dot-dash segment is an extrapolation from the data. The dotted curve is our estimate of the spectrum for two-electron shake off.

The most accurate measurement of the photoelectron spectrum from Ne was reported by Siegbahn *et al.* [see Fig. 4.1 in Ref. 4], and is presented schematically in Fig. 1. The origin of each of the peaks in our figure is described in Table I. Comparison between the original spectrum and the schematic representation of Fig. 1 demonstrates some of the difficulties in extracting spectroscopic factors even from data as detailed as those of the ESCA experiment. The original plot of the spectrum in Ref. 4 had three peaks (labeled there numbers 2, 3, and 4) due to inelastic scattering of electrons which left the ion in the single-hole ground state. They should be added to the strength of the 0 peak (the state we have denoted by $\alpha = 0$ and given by the peak denoted 0 in Fig. 1). Peaks 1, 5, and 6 of the original data, as well as those to the right of the 0 peak, must be discarded since they result from satellite x rays in the incident beam. Peaks 7–12 are due to shake up and, therefore, contribute to the sum determining the rearrangement energy.

However, before we can extract their spectroscopic factors, we must know whether the removal is sudden. From the data of Carlson and Krause[9] (see Fig. 1 of their paper), we see that at 1.354 keV, the energy of the Mg *Kα* x ray used in the ESCA experiment,[4] we have approached the sudden limit to within better than 3%. Thus, we may expect a small underestimate for the rearrangement energy.

We also must determine what part of the photoionization cross section represents shake-off electrons. The probability of single-electron shake off was measured to be 16%.[10,11] Double and higher shake off is about 4%.[9,11] Using these numbers together with the relative strengths of the shake-up peaks as given in Table I, we find 6% probability for shake up and 74% probability for leaving the ion in the single-hole state.

The energy spectrum of the single shake-off electrons[10] (with the same x rays as in Ref. 4) is presented schematically in Fig. 1. Numerical integration from Fig. 1 gives a centroid for the single shake-off electrons of about 90 eV relative to the single-hole peak $S_{1s}(\infty)$. Our estimate for the center for double and higher shake off is double shake-off threshold plus 55 eV, i.e., ~120 eV. Inserting these values in the equation for the rearrangement energy, Eq. (3.5), gives $\Delta_{1s} = 0.06 \times 40 + 0.16 \times 90 + 0.04 \times 120 = 22$ eV. The value determined from comparing HF calculations with method A and method B is 24 eV[3,12] (cf. the solid curve in Fig. 2), in very good agreement with the value we infer from the data. Our approximate formula, plotted in Figs. 2 and 3, Eq. (5.14), also agrees within 1 eV with this result. A recent determination of Δ_{1s}, based on a similar analysis of Manne and Åberg,[8] gave only 16 eV, probably because it referred only to a restricted part of the Ne spectrum.

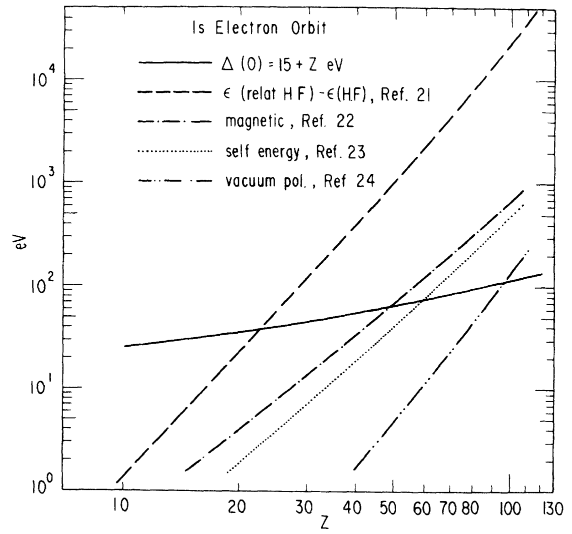

FIG. 2. Comparison of the magnitude of various corrections to nonrelativistic HF 1*s* electron energies calculated for finite nuclear charge distributions. The curve for Δ(0) is a fit to the calculated points as given in Fig. 3.

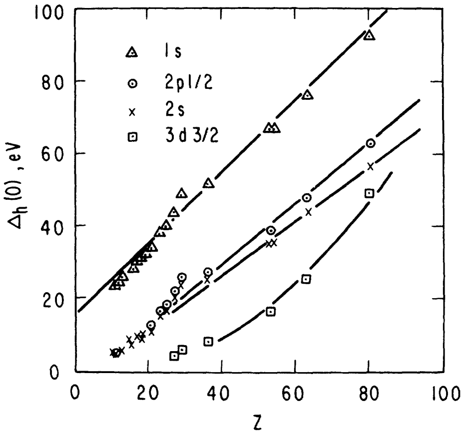

FIG. 3. Rearrangement energies from relativistic HF calculations in Refs. 2, 3, and 12.

The reduction of shaking probability as the removal goes from the sudden toward the adiabatic limit was demonstrated by the experiments of Carlson and Krause.[9] The intermediate situation is estimated to be reached with 0.97-keV x rays, namely, 100 eV above threshold or "absorption edge." Removal of a 1*s* electron with this energy leaves the residual ion with only one-half as much shaking or excitation in addition to the 1*s* hole. The rearrangement energy as defined above is also about one-half its maximum value $\Delta_{1s}(0)$. Such variations of the x-ray energy from the threshold to the point of approximate saturation of shaking allow a measurement of the characteristic time constants in the rearrangement process.

V. CALCULATION OF REARRANGEMENT ENERGIES AND PHOTO-IONIZATION THRESHOLDS FOR ATOMS

The features of atomic structure which we have discussed in the preceding sections can be calculated in the HF approximation. Adding recent results on various corrections to HF then allows us to predict rearrangement energies and thresholds within a few eV. For the outer electrons, correlations are the dominant correction. The order of magnitude is given by $E_{\mathrm{corr}}/Z \approx -(1.306 + 0.585 \ln Z)$eV.[13] A comprehensive review of recent theoretical approaches to correlation energies is given in Ref. 14. The major deviations from nonrelativistic HF for inner electrons are shown in Fig. 2, which refers to the 1s-electron orbit.

The solid curve in Fig. 2 is a fit to the rearrangement energy calculated with relativistic HF (cf. Fig. 3). It is the result of a variational calculation for the removal threshold relative to the HF eigenvalue.

At this point we want to specify our terminology by briefly reviewing the essentials of the HF variation. The eigenvalue there is a Lagrange multiplier in a variational determination of the energy where the space of admissible functions consists of Slater determinants of orthonormal single-particle wave functions. To first order in the two-body interaction v, the HF energy is

$$E^{\mathrm{HF}}[\{\varphi_i\}]=\sum_{i=1}^{N}\left(\varepsilon_1[\varphi_i]+\tfrac{1}{2}\varepsilon_v[\varphi_i,\{\varphi_{j\neq i}\}]\right) . \tag{5.1}$$

This is a functional of a set $\{\varphi_i\}$, where

$$\varepsilon_1[\varphi_i]=\int d^3x\left[\left(\frac{\partial\varphi_i}{\partial x}\right)^2+V(x)\varphi_i^2(x)\right], \tag{5.2}$$

$$\varepsilon_v[\varphi_i,\{\varphi_{j\neq i}\}]=\sum_{j=1}^{N}\int d^3x d^3x'[\varphi_i^2(x)v(x,x')\varphi_j^2(x') - \varphi_i(x)\varphi_j(x')v(x,x')\varphi_j(x)\varphi_i(x')] . \tag{5.3}$$

Restriction to a space of N orthonormal φ's is taken into account by N constraining functionals in a given φ_i variation

$$C[\varphi_i,\{\varphi_j\}]=\int dx\,\varphi_i(x)\varphi_j(x)-\delta_{ij} \equiv\int dx\,c_{ij}(x)=0 , \qquad j=1,\ldots,N . \tag{5.4}$$

The optimal φ_i is determined from

$$\frac{\delta}{\delta\varphi_i}\left(E^{\mathrm{HF}}[\{\varphi_i\}]-\sum_{i,j=1}^{N}\lambda_{ij}C[\varphi_i,\{\varphi_j\}]\right)=0 , \tag{5.5}$$

where λ_{ij} are the Lagrange multipliers for the constraining functional C. Substituting Eq. (5.1) into Eq. (5.5) gives

$$\left(-\frac{\partial^2}{\partial x^2}+V(x)\right)\varphi_i(x)+\sum_{j\neq i}^{N}\left(\int d^3x'[\varphi_i(x)v(x,x')\varphi_j^2(x') -\varphi_j(x')v(x,x')\varphi_j(x)\varphi_i(x')]-\lambda_{ij}\varphi_j(x)\right)=\lambda_{ii}\varphi_i(x) . \tag{5.6}$$

We fulfill the constraint (5.4) by *choosing* the set of Lagrangian parameters to be $\lambda_{ij}=\epsilon_i\delta_{ij}$, since we can prove straightforwardly that the above equation with this choice, i.e.,

$$\left(-\frac{\partial^2}{\partial x^2}+V(x)\right)\varphi_i(x)+\sum_{j\neq i}^{N}\int d^3x'[\varphi_i(x)v(x,x')\varphi_j^2(x') -\varphi_j(x')v(x,x')\varphi_j(x)\varphi_i(x')]=\epsilon_i\varphi_i(x) , \tag{5.7}$$

yields orthogonal functions φ_i which are normalizable for certain (at least N "eigen") values ϵ_i—if v is physically appropriate.

As we have shown in Sec. III, the eigenvalues should not be compared with the lowest missing-energy peaks or removal thresholds. The thresholds are determined variationally by comparing the above ground-state energy [from Eq. (5.1) using the self-consistent solutions φ_i of Eq. (5.7)] with another variationally determined first-order energy, namely, the "excited" state energy of an $(N-1)$-Fermion system obtained by putting a hole at a previously occupied level, i.e., by requiring one φ, say φ_1, to have zero norm. In this case, we have the orthonormality constraints

$$C'[\varphi_{i\neq1},\{\varphi_{j\neq1}\}]=\int dx\,\varphi_i(x)\varphi_j(x)-\delta_{ij}=0 , \qquad j=2,\ldots,N \tag{5.8}$$

plus the hole constraint

$$C'[\varphi_1,\varphi_1]=\int dx\,\varphi_1^2(x)=0 . \tag{5.9}$$

By the fundamental theorem of variational calculus, this latter constraint implies that φ_1 vanishes everywhere, i.e., φ_1 "cannot be varied." For the other values of i, j the variational derivation is identical to the steps leading to Eq. (5.7) with φ_1 being always zero. The extremal energy for Slater determinant wave functions fulfilling the hole constraint (5.9) is, therefore, obtained by self-consistently solving a system of Eqs. (5.7) with $\varphi_1\equiv0$.

The threshold for removal of a particle in the orbit "1" is, of course, the difference of the total energies, computed with the two extremal sets $\{\varphi\}$ from two differently constrained variations as described above. An inconsistent and unsymmetrical approximation in this framework would to be take for the second, i.e., the $N-1$ system, the first extremal set with $\varphi_1=0$. Then the removal energy is simply ϵ_1, the first term in Eq. (5.10) below, the latter result often being defined as Koopmans's theorem; although this definition does not give full credit to Koopmans's work. The correct expression using Eq. (3.10) is

$$\epsilon_1+\Delta_1(0)=E(N)-E^{0_h}(N-1) =\epsilon_1+\sum_{i\neq1}(\epsilon_i-\epsilon_i')-\sum_{j\neq1}v_{1j}-\tfrac{1}{2}\sum_{i,j\neq1}(v_{ij}-v_{ij}') . \tag{5.10}$$

If the changes in the wave function $\Delta\varphi_1$ and in the eigenvalues $\Delta\epsilon_i$ are defined by the equations

$$\Delta\epsilon_i\equiv\epsilon_i-\epsilon_i', \quad \Delta\varphi_i\equiv\varphi_i-\varphi_i' , \tag{5.11}$$

it can be shown that

$$\begin{aligned}\Delta_1 = &\sum_{i\neq1} \Delta\epsilon_i \Delta\varphi_i(x)\varphi_i(x)d^3x \\ &-\sum_{i\neq1} \int d^3x\, d^3x'\{\Delta\varphi_i(x)\varphi_1(x')v(x-x')[\varphi_1(x')\varphi_i(x)-\varphi_i(x')\varphi_1(x)]\} \\ &-\sum_{i,j\neq1} \int d^3x d^3x'\{\Delta\varphi_i(x)\Delta\varphi_j(x')v(x-x')[\varphi_j(x')\Delta\varphi_i(x)-\varphi_j(x)\Delta\varphi_i(x')]\} \\ &+\tfrac{1}{2}\sum_{i,j\neq1} \int d^3x d^3x'\{\Delta\varphi_i(x)\Delta\varphi_j(x')v(x-x')[\Delta\varphi_j(x')\Delta\varphi_i(x)-\Delta\varphi_j(x)\Delta\varphi_i(x')]\}\ . \qquad (5.12)\end{aligned}$$

After the removal of an inner electron, each electron in the ion sees one more charge than in the atom. We schematically represent the screening of each electron by imagining that each electron in succession screens another charge. Then for hydrogenlike wave functions,

$$\varphi_i \sim (Z-i+1)^{3/2}\ , \quad \varphi_i' \sim (Z-i+2)^{3/2}$$

and

$$\epsilon_i \sim (Z-i+1)^2, \qquad \epsilon_i' \sim (Z-i+2)^2\ .$$

This gives

$$\int \varphi_i \Delta\varphi_i d^3x \sim 1/(Z-i+1)\ ,$$

$$\Delta\epsilon_i \sim Z-i+1\ ,$$

$$\int \Delta\varphi_i \Delta\varphi_i d^3x \sim 1/(Z-i+1)^2\ .$$

Therefore, we have

$$\Delta_1 = C_1 Z + C_2 + C_3 Z^{-1} + C_4 Z^{-2} + O(Z^{-3})\ . \qquad (5.13)$$

The constants C_3 and C_4 arise from terms which are third and fourth order in the small quantities $\Delta\varphi_i$ so we expect them to be small.

Therefore, for the removal of an inner electron, Δ_1 should be a linear function of the nuclear charge Z. Figure 3 shows a plot of the Δ_1 determined by SCF calculations[2,3,12] as a function of Z for several of the inner levels. For the $1s$, $2s$, and $2p_{1/2}$ (and $2p_{3/2}$, not shown in the figure), there is a linear dependence on Z. Of course, we would expect some deviations from a strict linear dependence and this seems to be particularly strong for Cu ($Z=29$). For the $3d_{3/2}$ level, the linear dependence no longer seems to hold. As can be seen in Fig. 3, the formula

$$\Delta_{1s}(0) = Z + 15 \text{ eV} \qquad (5.14)$$

fits the values for the $1s$ orbit to about ± 3 eV. This linear dependence of the rearrangement energy on Z differs from previous estimates. Brenner and Brown[5] claimed Δ_h was independent of Z, whereas Serber and Snyder[6] determined a $Z^{1/3}$ behavior from the Thomas-Fermi model.

VI. CONCLUSIONS

In this paper we have discussed the concept of a separation energy which depends on the speed of removal. It is the properly gauged centroid energy in single-particle transfer spectra. This concept allows a unified description of certain features exhibited in electron- as well as nucleon-removal data.[15,16] We have shown the following.

(i) This centroid moves from the threshold to a single-particle eigenvalue as the experimental setup is switched from adiabatic to sudden transfers. The threshold is also called the "absorption edge" or "mass difference" and is given by the peak with the lowest missing or excitation energy in the removal spectrum for the specified particle.

(ii) The shift in the centroid energy is the result of rearrangement in the residual system. If the particle is removed suddenly, the system is "shattered" and no rearrangement energy is passed on. Thus the maximum extra energy a particle can pick up in a slow removal is the difference of the eigenvalue and the lowest missing energy peak.

(iii) In practice, a very detailed measurement of the spectrum is required in order to allow a determination of centroids. We treated an atomic example which, in fact, was the only one we could find with practically sufficient spectrum measurements. Also, all quantitative theoretical questions were settled in that case to about 1 eV. An important result was that the shake off or *continuum part of the spectrum plays a major role* in shifting the centroid to the single-particle eigenvalue. In this example, the centroid shift due to shake up, i.e., discrete states, is only 2.4 eV of the total 22 eV. Centroids determined from discrete states alone can, therefore, at best establish lower limits on the amount of rearrangement when compared with the lowest missing-energy peak. That is, this peak, the removal threshold, is always of significance in comparisons with theory, whereas centroids of incomplete spectra, as usually obtained from nucleon transfer experiments, are of dubious value.

We have shown that agreement of a mass-difference calculation, for instance, the method B result of Refs. 2, 3, and 12, with the position of the lowest missing-energy peak or absorption edge indicates the applicability of the many-body formalism. However, nothing can be inferred about the rearrangement time of the system from such an agreement. The degree of relaxation involved in a given removal case can be determined from the *difference* of the centroid position and the lowest missing-energy peak. However, it would be incorrect to conclude that removals were adiabatic for inner and sudden for outer electrons just because threshold peaks agree better with method B and A results in the two respective regions.[2]

Obviously, the strength of the threshold peak decreases when the centroid moves away from it as removals become less and less adiabatic. This feature also seems to be present in nucleon-removal data. For example, MacFarlane[17] presented a compilation of neutron spectroscopic factors which indicates that the strength in the threshold peak does decrease with increasing removal speed (see Fig. 15 of Ref. 17). However, it is not easy to establish this trend quantitatively due to the many uncertainties in nuclear DWBA analysis. In addition, the determination of centroid energies is even more difficult than in the atomic case because there could be some very widely separated small components in the removal spectrum due to strong short-range repulsion in the NN interaction.[18]

A quantitative description of nucleon removals cannot be made in the HF framework outlined above. A "renormalized" HF is required and partial occupation probabilities must be considered. For this reason, the symmetrical expression[19] $\langle N|a_k H a_k^\dagger - a_k^\dagger H a_k|N\rangle$ seems to be more useful than Eq. (3.6). Here, the index k is no longer restricted to refer to particles below the Fermi surface. In the limit of pure HF, we have

$$\langle N|a_k H a_k^\dagger - a_k^\dagger H a_k|N\rangle - E(N)\,\mathrm{sgn}(k-F)$$

$$= \sum_\beta |\langle N+1,\ \beta_k|a_k^\dagger|N\rangle|^2 [E^{\beta_k}(N+1) - E(N)]$$

$$- \sum_\alpha |\langle N-1,\ \alpha_k|a_k|N\rangle|^2 [E^{\alpha_k}(N-1) - E(N)] \tag{6.1a}$$

$$= \epsilon_k\ , \tag{6.1b}$$

where $\mathrm{sgn}(k-F)$ is $+1$ or -1 for k referring to levels above or below the Fermi surface [cf. Eq. (3.9)].

An attempt to establish a HF-type formalism was made by defining the nuclear single-particle potential to have the "observable" right-hand side of Eq. (6.1a) as eigenvalues.[20] A discussion of "renormalized" nuclear HF potentials and rearrangement effects will be given in a separate paper. We expect the qualitative features of the present results to be observable also in nuclear spectra.

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Auto-Ionization of H_2 near Threshold

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The purpose of this paper is to show by a model calculation that the internal conversion theory may be used to obtain auto-ionization rates for $\Delta\nu_{if} = 1$ vibrational transitions in H_2, within the right order of magnitude. Thus, the present calculation remedies the apparent inability of the model to predict desirable rates as calculated by previous authors. The results obtained compare fairly well with the experimental estimates of Chupka and Berkowitz, but are closer to the alternative theoretical calculations of Berry and Nielsen for $\Delta\nu_{if} = 1$. It explicitly shows the $1/n^3$ dependence of rates for increasing principal quantum numbers n, and follows the so-called "propensity rule" for vibrational transitions involved. Limitations and possible refinements of the present model are discussed, and the generalization for molecules other than H_2 is indicated. Within the approximation of the model, it provides a simple formula from which rates may be easily estimated.

I. INTRODUCTION

In molecular H_2, if one of the electrons is removed sufficiently away from the nucleus, it may be considered to move in an approximate Rydberg state around the residual H_2^+ ion core. High-resolution experiments[1-3] on photo-ionization and photoabsorption have not only confirmed the presence of such states for H_2 but have also yielded quantitative rates of auto-ionization from these states. The results further reveal that the auto-ionization process, in fact, dominates over the photo-ionization process in the neighborhood of the threshold of ionization. Several theoretical calculations[4-7] have already been done to estimate the auto-ionization from these states. In the first kind of calculations, initiated by Berry,[4] the auto-ionization is assumed to be mediated by the nuclear kinetic-energy terms which break down the Born-Oppenheimer separation by coupling the core vibrations with the electron motion. In the second kind of model, first used for the present purpose by Russek *et al.*,[5] the energy of vibration is assumed to be mediated to the Rydberg electron directly through the internal conversion process, much used in nuclear problems before.[8] Recently, Ritchie[9] has calculated rates of auto-ionization within a semiclassical model, which are in qualitative agreement with experimental estimates for high-vibrational states with single-quantum transitions.

In their first applications, the initial theories[4,5] failed to produce the experimental rates by falling short by an order of magnitude or more. Subsequently, however, the calculations of Berry and Nielsen[6,7] using detailed adiabatic molecular calculations have improved the results to within a few times the experimental results.

The experimental estimates[2] may be uncertain within a factor of 2 or so and it may be considered that the nonadiabatic model is adequate enough to describe the auto-ionization process. However, due to the very nature of the theory, extensive numerical calculations are necessary to arrive at the estimates. The internal conversion model, on the other hand, is attractive for its simplicity and would be useful if the model could be shown to yield the appropriate rates.

From results of calculations within nonadiabatic models[7] it has emerged that the monopole nuclear interaction is principally responsible for transmission of vibrational energy to the Rydberg electron. It has been previously demonstrated by Russek *et al.*[5] that there is an essential equivalence between the nonadiabatic and the internal conversion