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Atomic Central-Field Models for Open Shells with Application to Transition Metals*

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Ensemble averages are used to define energy functionals for open-shell atoms. Orbital equations and effective potentials for a Hartree-Fock procedure are derived and compared to the hyper-Hartree-Fock method. Total energies and orbitals have been calculated for the atoms Cr, Fe, Co, and Ni. Effective interaction parameters for valence-shell electrons are defined and evaluated.

I. INTRODUCTION

Self-consistent-field calculations for transition-metal atoms are presented in this paper. They are based on energy expressions obtained as ensemble averages allowing a convenient treatment of several open shells. The results resemble those obtained by Slater and co-workers within the so-called hyper-Hartree-Fock method[1] but differ in certain aspects. Particularly, it is not borne out in the present calculations that configurations with fractional occupation numbers are more stable than normal configurations.

Atomic central fields have been studied since the conception of quantum mechanics and numerous different calculational schemes have evolved. The remarkable simplicity of the Fermi-Thomas statistical model of the atom[2] and the success of its predictions concerning the electronic structure of all elements in the periodic system provides strong support for the concept of a universal central field and the independent particle model for the electrons. The theory of complex spectra as originated by Slater[3] is similarly founded on the idea of a central field, which defines a set of one-electron states transforming according to the three-dimensional rotation group, common to a number of terms derived from the same configuration. Such a central field is defined by the statistical model and by the self-consistent-field procedure designed by Hartree.[4] The latter field is obtained from a spherical average of the electronic charge distribution in the atom excluding the contribution from one electron in the subshell for which the potential applies. This prescription results in a potential for a neutral atom which has a Coulombic asymptotic form at large distances from the atomic nucleus.

A defect of the statistical central field and of Hartree's self-consistent field is the lack of an exchange potential accounting for the Fermi statistics of electrons. This is remedied in the Hartree-Fock method where an energy functional is calculated from an antisymmetric wave function corresponding to a term of a configuration. The calculation of the functional involves symmetry and equivalence restrictions on the one-electron states as discussed by Nesbet.[5] These restrictions lead to the occurrence of off-diagonal Lagrangian multipliers in the integrodifferential equations determining the one-electron states, and to certain complications when applying many-electron perturbation theory with Hartree-Fock solutions as the zeroth-order unperturbed states, since Brillouin's theorem[6] is not applicable.

Atomic orbitals are extensively used for the calculation of molecular and crystalline electronic properties and it has been a matter of discussion what atomic basis set to use in such applications. Slater[7] has argued that it would be appropriate to use orbitals obtained from an energy functional formed as a weighted mean over all multiplets arising from a given configuration. This may be interpreted as a simulation of an "atom in a molecule" where the surrounding atoms cause perturbations which destroy the multiplet structure; the total orbital and spin angular momenta are no longer good quantum numbers. The averaging procedure does not remove the necessity for off-diagonal Lagrangian multipliers.

The notion of an atom in a molecule[8] leads one to consider the possibility of energy functionals which are obtained as averages over multiplets from configurations with varying number of electrons in the different subshells. The number of electrons in the atom is then no longer a good quantum number and ionic states are contributing to the average. Section II contains a discussion of such average formation based on the statistical-mechanical concept of an ensemble. Variation of the energy functionals is discussed in Sec. III, and it is shown that off-diagonal Lagrangian multipliers can be eliminated for a particular type of ensemble. Calculational results are presented for chromium, iron, cobalt, and nickel in Sec. IV. These results are used in Sec. V to discuss the concepts of differential ionization energies and effective interactions in a valence shell. Our concluding remarks are collected in Sec. VI.

II. ENERGY EXPRESSION FOR ENSEMBLES

The language of second quantization will be used here. Electron field operators $\psi(x)$ and $\psi^\dagger(x)$ are expressed in terms of an orthonormal basis,

$$\psi(x)=\textstyle\sum_s u_s(x)\, a_s \ , \tag{1}$$

$$\psi^\dagger(x)=\textstyle\sum_s u_s^*(x)\, a_s^\dagger \ , \tag{2}$$

which is adapted to central symmetry. The annihilation operators a_s anticommute among themselves as do the creation operators $a_s^\dagger$, while we have the relation

$$\begin{aligned} a_s a_t^\dagger + a_t^\dagger a_s &= [a_s, a_t^\dagger]_+ \\ &= \int dx\, u_s^*(x) u_t(x) = (s\,|\,t) = \delta_{st} \ . \end{aligned} \tag{3}$$

The Hamiltonian for a system of noninteracting electrons is

$$H_0=\sum_{st} a_s^\dagger h_{st} a_t \ , \tag{4}$$

or, if the basis is chosen appropriately,

$$H_0=\textstyle\sum_s \epsilon_s n_s \ , \tag{5}$$

where the occupation number operators $n_s=a_s^\dagger a_s$ commute with one another and are idempotent,

$$n_s^2=n_s \ . \tag{6}$$

The statistical mechanics of such a system can be determined by a study of the grand canonical partition function

$$Z=\mathrm{Tr}\, e^{-(H_0-\mu N_{\mathrm{op}})/\Theta} \ , \tag{7}$$

where Θ is the absolute temperature in energy units, μ is the chemical potential, and N_{op} is the number operator

$$N_{\mathrm{op}}=\textstyle\sum_s n_s \ . \tag{8}$$

The related density operator is

$$\rho=Z^{-1} e^{-(H_0-\mu N_{\mathrm{op}})/\Theta} \ , \tag{9}$$

and the average value of an operator A is calculated as

$$\langle A\rangle=\mathrm{Tr}\, A\rho \ . \tag{10}$$

The density operator for a case of noninteracting electrons in the representation where H_0 is given by Eq. (5) will, due to the properties of the occupation number operators, occur as a product

$$\rho=\textstyle\prod_s [(1+\lambda_s n_s)/(2+\lambda_s)] \ . \tag{11}$$

Each factor is normalized in the two-dimensional space spanned by the eigenstates of the corresponding n_s, and thus

$$\mathrm{Tr}\,\rho=1 \ . \tag{12}$$

The parameter λ_s is obtained as

$$\lambda_s=e^{-(\epsilon_s-\mu)/\Theta} -1 \ . \tag{13}$$

We see that the average occupation of the state s is given by the Fermi distribution law,

$$\langle n_s\rangle=(1+\lambda_s)/(2+\lambda_s)=(1+e^{\epsilon_s-\mu/\Theta})^{-1} \ . \tag{14}$$

It should be noted that Eq. (14) gives a unique way of defining the density operator (11) from a given set of occupation numbers $\langle n_s\rangle$,

$$\rho=\textstyle\prod_s [1-\langle n_s\rangle+(2\langle n_s\rangle-1)n_s] \ , \tag{15}$$

and that reference to thermodynamical parameters is no longer necessary. We will in what follows consider ensembles of the type (15) which cannot be related to equilibrium situations in statistical mechanics but are purely formal devices for the formation of averages over certain manifolds of many-electron states.

An ensemble of the form (15) will generally result in a nonzero width of the number operator for electrons. It follows from Eq. (15) that the average value of a product of occupation number operators equals the product of the averages,

$$\langle n_s n_t\rangle=\langle n_s\rangle\,\langle n_t\rangle \ , \tag{16}$$

$$\begin{aligned} \langle N_{\mathrm{op}}^2\rangle &= \sum_s \langle n_s\rangle + \sum_{s\neq t} \langle n_s\rangle\langle n_t\rangle \\ &= \langle N_{\mathrm{op}}\rangle^2 + \sum_s \langle n_s\rangle(1-\langle n_s\rangle) \ , \end{aligned} \tag{17}$$

which shows the obvious fact that only for occupation numbers that are either zero or unity does the ensemble correspond to a pure state for the number operator. Otherwise the width is

$$\langle (N_{\mathrm{op}}-\langle N_{\mathrm{op}}\rangle)^2\rangle^{1/2}=[\textstyle\sum_s \langle n_s\rangle(1-\langle n_s\rangle)]^{1/2} \ . \tag{18}$$

The density operator (15) commutes with the number operator and by means of a complete set of projectors P_N corresponding to eigenvalues N of the number operator we can write

$$\rho=\textstyle\sum P_N \rho \ , \tag{19}$$

where each term can be used, after normalization, as a type of canonical ensemble, with zero width for the number operator. A convenient realization of the projectors is the form

$$P_N=\int_0^1 dt\, e^{2\pi i t(N_{\mathrm{op}}-N)} \ , \tag{20}$$

which satisfies the required relations

$$(N_{\mathrm{op}}-N)P_N=0 \ , \tag{21}$$

$$P_N^2=P_N \ , \tag{22}$$

and

$$\textstyle\sum_N P_N=1 \ , \tag{23}$$

as well as being Hermitian.

A projected density operator like

$$\rho_N = P_N \rho / (\mathrm{Tr} P_N \rho) \tag{24}$$

will no longer have simple relationships, as in the left-hand equality of Eq. (14), between average values $\langle n_s \rangle_N = \mathrm{Tr} n_s \rho_N$ and the parameters λ_s, as will be seen in the applications to transition metal atoms. It is a straightforward procedure to calculate the average values from a set of λ's using the given representations of P_N and ρ, and we note that the factorization property (16) does not hold when the projected density operator is used.

Energy functionals can now be derived for interacting electronic systems by taking average values of the total Hamiltonian with respect to the density operators given by Eqs. (11), (15), and (24). The general expression in second quantization for the Hamiltonian is

$$H = \sum_{st} a_s^\dagger h_{st} a_t + \tfrac{1}{2} \sum_{sts't'} (st|s't') a_s^\dagger a_{s'}^\dagger a_{t'} a_t \ , \tag{25}$$

where the explicit form for electron interaction matrix elements $(st|s't')$ will be given later and in detail for central field orbitals. The average value of the energy, $\langle H \rangle$ or $\langle H \rangle_N$, is then expressed in terms of average values of simple products of creation and annihilation operators:

$$\langle a_s^\dagger a_t \rangle = \delta_{st} \langle n_s \rangle \ , \tag{26}$$

$$\langle a_s^\dagger a_t \rangle_N = \delta_{st} \langle n_s \rangle_N \ , \tag{27}$$

$$\langle a_s^\dagger a_{s'}^\dagger a_{t'} a_t \rangle = (\delta_{st} \delta_{s't'} - \delta_{st'} \delta_{s't}) \langle n_s \rangle \langle n_{s'} \rangle \ , \tag{28}$$

$$\langle a_s^\dagger a_{s'}^\dagger a_{t'} a_t \rangle_N = (\delta_{st} \delta_{s't'} - \delta_{st'} \delta_{s't'}) \langle n_s n_{s'} \rangle_N \ . \tag{29}$$

Off-diagonal elements vanish due to the direct product form of ρ and P_N but there is no factorization of expectation values in Eq. (29). It obtains that

$$\langle H \rangle = \textstyle\sum_s h_{ss} \langle n_s \rangle + \tfrac{1}{2} \sum [(ss|tt) - (st|ts)] \langle n_s \rangle \langle n_t \rangle \tag{30}$$

and

$$\langle H \rangle_N = \textstyle\sum_s h_{ss} \langle n_s \rangle_N + \tfrac{1}{2} \sum [(ss|tt) - (st|ts)] \langle n_s n_t \rangle_N \ . \tag{31}$$

We specify in the following our notation in order to make use of the spherical symmetry. State label s is a compound notation for the set of four quantum numbers $(nlm\sigma)$, the principal, orbital angular momentum, magnetic, and spin quantum numbers, respectively. The ensemble density operators are invariant under rotations of the coordinate system only if the parameters $\lambda_{(nlm\sigma)}$ are independent of m and σ. We put

$$\langle n_{(nlm\sigma)} \rangle = q(nl)/(4l+2) \ , \tag{32}$$

so that $q(nl)$ equals the average number of electrons in the subshell (nl). The one-electron integrals in the Hamiltonian are similarly such that

$$h_{(nlm\sigma)(nlm\sigma)} = I(nl) \ , \tag{33}$$

where Slater's notation[9] is employed.

The electron interaction integrals are obtained in terms of $3j$ symbols and Slater integrals R^k as

$$\begin{aligned}
&(n_1 l_1 m_1 \sigma_1, n_2 l_2 m_2 \sigma_2 | n_3 l_3 m_3 \sigma_3, n_4 l_4 m_4 \sigma_4) \\
&\quad = \delta_{\sigma_1\sigma_2} \delta_{\sigma_3\sigma_4} (-)^{-m_1-m_4} \sum_{k\mu} \begin{pmatrix} l_1 & k & l_2 \\ -m_1 & \mu & m_2 \end{pmatrix} \begin{pmatrix} l_4 & k & l_3 \\ -m_4 & \mu & m_3 \end{pmatrix} \begin{pmatrix} l_1 & k & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_4 & k & l_3 \\ 0 & 0 & 0 \end{pmatrix} \\
&\qquad \times [(2l_1+1)(2l_2+1)(2l_3+1)(2l_4+1)]^{1/2} R^k(n_1 l_1 n_3 l_3, n_2 l_2 n_4 l_4) \ .
\end{aligned} \tag{34}$$

There will only occur F^k and G^k integrals[9] in the energy formula since either is $(n_1 l_1)$ equal to $(n_2 l_2)$ and $(n_3 l_3)$ equal to $(n_4 l_4)$ or similar relations hold with 2 and 4 permuted. The two-electron operator average value $\langle n_s n_t \rangle_N$ will be given in terms of a new quantity

$$\langle n_{(n_1 l_1 m_1 \sigma_1)} n_{(n_2 l_2 m_2 \sigma_2)} \rangle_N = Q(n_1 l_1 n_2 l_2)/[(4l_1+2)(4l_2+2)] \ , \tag{35}$$

where it should be noted that the definition of $Q(nl, nl)$ derives from a case where $(m_1 \sigma_1)$ differs from $(m_2 \sigma_2)$. The term corresponding to equal indices occurs in the energy expectation value with zero coefficient so we can sum freely over m's and σ's after having introduced the expression (35).

The summation in the electron interaction term in the energy functional over magnetic and spin quantum numbers leads to the definition of average interaction parameters that we will denote $V(nl, n'l')$ and which are defined as

$$V(nl, n'l') = F^0(nl, n'l') - \tfrac{1}{2} \textstyle\sum_k \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 G^k(nl, n'l') \ . \tag{36}$$

These parameters equal the ones used by Slater and denoted $(nl, n'l')^1$ apart from intrashell interactions where they differ by a factor such that

$$V(nl, nl) = (4l+1)(nl, nl)/(4l+2) \ . \tag{37}$$

The final formulas for the energy functionals are then

$$\langle H\rangle=\sum_{nl} I(nl)\,q(nl)+\tfrac{1}{2}\sum_{nln'l'} q(nl)\,q(n'l')\,V(nl,n'l') \tag{38}$$

and

$$\langle H\rangle_N=\sum_{nl} I(nl)\,q(nl)+\tfrac{1}{2}\sum_{nln'l'} Q(nl,n'l')\,V(nl,n'l') \ , \tag{39}$$

where $q(nl)$ in the last expression refers to an average $\langle\ \rangle_N$ in Eq. (32). The main difficulty in the computation of the $Q(nl,n'l')$ arises from the rather complex relations between them and the $q(nl)$. Only in the case of one partially filled subshell is there a simple relation,

$$\begin{aligned}Q(nl,n'l')&=q(nl)\,q(n'l')\\&\quad-\delta_{nn'}\,\delta_{ll'}\,q(nl)\,[4l+2-q(nl)]/(4l+1)\ ,\end{aligned} \tag{40}$$

which in this case makes the energy expression identical to the one given by Slater for one open subshell.[9] It should be noted that for the case of several open subshells, even if the corresponding $q(nl)$ are integers, the energy expression differs from that of Slater since the density operator ρ_N is not an eigenoperator to the subshell number operator,

$$N_{(nl)}=\sum_{m\sigma} n_{(nlm\sigma)}\ . \tag{41}$$

We feel that the energy functional $\langle H\rangle_N$ is particularly suited for the discussion of configurations with fractional occupation numbers since in such cases one cannot use density operators which are eigenoperators to subshell number operators.

The basis functions have the form

$$u_{(nlm\sigma)}=[P_{nl}(r)/r\,]\,Y_{lm}(\theta,\varphi)\,\delta_{\sigma\zeta}\ , \tag{42}$$

in polar coordinates and the spin variable ζ. Potential functions are given in the notation

$$\begin{aligned}\varphi_k(nl,n'l';r)&=r^{-k-1}\int_0^r dr'\,(r')^k P_{nl}(r')P_{n'l'}(r')\\&\quad+r^k\int_r^\infty dr'\,(r')^{-k-1}P_{nl}(r')\,P_{n'l'}(r')\ ,\end{aligned} \tag{43}$$

and we obtain the functional derivative of the first energy expression $\langle H\rangle$ of Eq. (38) in atomic units as

$$\begin{aligned}\delta\langle H\rangle/\delta P_{nl}(r)&=q(nl)\,[-\tfrac{1}{2}P''_{nl}(r)+\tfrac{1}{2}l(l+1)\,r^{-2}P_{nl}(r)-(Z/r)\,P_{nl}(r)\\&\quad+\sum_{n'l'} q(n'l')\,\varphi_0(n'l',n'l';r)\,P_{nl}(r)-\tfrac{1}{2}\sum_{n'l'k} q(n'l')\,\begin{pmatrix}l&k&l'\\0&0&0\end{pmatrix}^2\varphi_k(n'l',nl;r)\,P_{n'l'}(r)]\\&=q(nl)\,F_l\,P_{nl}(r)\ ,\end{aligned} \tag{44}$$

where the notation F_l is used for the integrodifferential operator. It is the effective operator of the Hartree-Fock equations determining the radial factors $P_{nl}(r)$. The orthonormality constraints on the orbitals brings in Lagrangian multipliers $\epsilon(nl)$ and $\epsilon(nl,n'l)$ such that the final equations read

$$F_l\,P_{nl}(r)=\epsilon(nl)\,P_{nl}(r)+\sum_{n'\neq n}\epsilon(nl,n'l)\,P_{n'l}(r)\ . \tag{45}$$

The off-diagonal Lagrangian multipliers $\epsilon(nl,n'l)$ can be eliminated by choosing $P_{nl}(r)$ as the eigenfunctions of F_l.

The functional derivative $\delta\langle H\rangle_N/\delta P_{nl}(r)$ is conveniently expressed in terms of F_l, φ_k, and auxiliary parameters

$$A(nl,n'l')=Q(nl,n'l')/q(nl)-q(n'l')\ , \tag{46}$$

so that the Hartree-Fock equations for the radial factors becomes

$$\begin{aligned}F_l\,P_{nl}(r)&=\epsilon_N(nl)\,P_{nl}(r)+\sum_{n'\neq n}\epsilon(nl,n'l)\,P_{n'l}(r)\\&\quad-\sum_{n'l'}A(nl,n'l')\,\varphi_0(n'l',n'l';r)\,P_{nl}(r)\\&\quad+\tfrac{1}{2}\sum_{n'l'k}A(nl,n'l')\begin{pmatrix}l&k&l'\\0&0&0\end{pmatrix}^2\varphi_k(n'l',nl;r)\,P_{n'l'}(r)\ .\end{aligned} \tag{47}$$

In this case it is not possible to disregard the off-diagonal Lagrangian multipliers and we find that since

$$q(nl)\,\epsilon(nl,n'l)=q(n'l)\,\epsilon(n'l,nl)\ , \tag{48}$$

then

$$\begin{aligned}\epsilon(nl,n'l)&=\sum_{n''l''}B(nl,n'l,n''l'')\,[R^0(n'ln''l'',nln''l'')\\&\quad-\tfrac{1}{2}\sum_k\begin{pmatrix}l&k&l''\\0&0&0\end{pmatrix}^2R^k(n'ln''l'',n''l''nl)]\ ,\end{aligned} \tag{49}$$

where

$$\begin{aligned}B(nl,n'l,n''l'')&=q(n'l)\,[A(nl,n''l'')\\&\quad-A(n'l,n''l'')]/[q(n'l)-q(nl)]\ .\end{aligned} \tag{50}$$

These expressions are the general ones but it should be noted that $A(nl,n'l')$ equals zero whenever one of the subshells (nl) or $(n'l')$ is either completely occupied or empty, so that the summation in Eq. (49) extends only over the partially filled subshells.

III. VARIATIONS OF ENERGY EXPRESSIONS

The functional derivative of the energy expressions derived in Sec. II with respect to the radial part of the basis orbitals leads to equations that are very similar to those obtained from average of configuration energy expressions. The latter are obtained from Eq. (39) by means of Eq. (40); thus it is only a simple matter of computing new coefficients for the Coulomb and exchange potentials in the integrodifferential equations for the radial factors in the orbitals and of using available computational programs for the evaluation of optimum orbitals. It is a consequence of the form (38) that there is no need for off-diagonal Lagrangian multipliers to ensure the orthogonality of the basis set since the potential will be the same for all orbitals. The same does not hold for the form $\langle H\rangle_N$ of Eq. (39), but the calculations for the orbitals are as simple as those for average of configuration functionals, while it is a slightly more complicated matter to compute the $Q(nl,n'l')$.

We will now assume that the orbitals have been determined such that variations of $\langle H\rangle$ in Eq. (38) with respect to the radial factors vanish and study the partial derivatives with respect to occupation numbers $q(nl)$:

$$\frac{\partial\langle H\rangle}{\partial q(nl)}=I(nl)+\sum_{n'l'} q(n'l')\,V(nl,n'l')=\epsilon(nl)\;. \tag{51}$$

The parameters $\epsilon(nl)$ which occur as eigenvalues for the radial equations are the orbital energies and are thus obtained as derivatives rather than energy differences as in Koopmans's[10] interpretation of orbital energies. Optimization of $\langle H-\mu N_{\mathrm{op}}\rangle$ leads to the conditions that

$$\frac{\partial(\langle H\rangle-\mu\langle N_{\mathrm{op}}\rangle)}{\partial q(nl)}=0\;, \tag{52}$$

while

$$0\leq q(nl)\leq 4l+2\;. \tag{53}$$

The Lagrangian multiplier μ appears similarly as the chemical potential in statistical mechanics and we see that it has a value such that it separates occupied from unoccupied orbital energy levels. The minimum total energy $\langle H\rangle$ is obtained when

$$\begin{aligned} &q(nl)=4l+2, && \epsilon(nl)<\mu\\ &q(nl)=0\;, && \epsilon(nl)>\mu\\ &0\leq q(nl)\leq 4l+2, && \epsilon(nl)=\mu \end{aligned} \tag{54}$$

and

$$\sum_{nl} q(nl)=\langle N_{\mathrm{op}}\rangle=N\;. \tag{55}$$

These relations are seen to lead to several open subshells only in the case when the corresponding orbital energies are degenerate.

For the case that the orbitals are optimized for the energy average $\langle H\rangle_N$ of Eq. (39) we have that the orbital energies which are derived from the radial equations are

$$\epsilon_N(nl)=I(nl)+\sum_{n'l'} Q(nl,n'l')\,V(nl,n'l')/q(nl)\;, \tag{56}$$

which is different from the partial derivative with respect to occupation number of energy functional $\langle H\rangle_N$. Thus there is no simple relation between the order of the orbital energy levels and the magnitude of the occupation numbers for the minimum-energy configuration. Neither is there a unique way of defining modified orbital energies, as is done in Ref. 1, from partial derivatives $\partial\langle H\rangle_N/\partial q(nl)$ since the different $q(nl)$ are not independent parameters.

We explore here the detailed calculation of the $Q(nl,n'l')$ for the case of a transition-metal atom with partially filled $3d$ and $4s$ subshells. Thus we choose a density operator of the form (19) where λ_{1s}, λ_{2s}, λ_{2p}, λ_{3s}, and λ_{3p} all are infinitely large, λ_{3d} and λ_{4s} are independent variables, and all other λ's have the value -1. Then we obtain that

$$q(1s)=q(2s)=q(3s)=2\;, \tag{57}$$

$$q(2p)=q(3p)=6\;, \tag{58}$$

$$q(3d)+q(4s)=N-18=\nu\;, \tag{59}$$

and that all other $q(nl)$ vanish. It also follows, as was pointed out above, that whenever one of the subshells (nl) and $(n'l')$ is empty or completely filled the corresponding $Q(nl,n'l')$ is given by the formula

$$Q(nl,n'l')=q(nl)\,q(n'l')\;. \tag{60}$$

In order to calculate the remaining quantities, $Q(3d,3d)$, $Q(3d,4s)$, and $Q(4s,4s)$, we define the generating function

$$\begin{aligned} Z_\nu=\mathrm{Tr}\int_0^1 dt\,\exp[&2\pi i t(N_{(3d)}+N_{(4s)}-\nu)\\ &+\alpha(3d)N_{(3d)}+\alpha(4s)N_{(4s)}]\;, \end{aligned} \tag{61}$$

which is proportional to $\mathrm{Tr}P_N\rho$ with

$$\alpha(nl)=\ln(1+\lambda_{nl})\;, \tag{62}$$

which should be compared to Eq. (13). This gives us

$$q(nl)=\frac{\partial\ln Z_\nu}{\partial\alpha(nl)} \tag{63}$$

and

$$\begin{aligned}\langle N_{(nl)}N_{(n'l')}\rangle_N&=\frac{Z_\nu^{-1}\,\partial^2 Z_\nu}{\partial\alpha(nl)\,\partial\alpha(n'l')}\\ &=q(nl)\,q(n'l')+\frac{\partial^2\ln Z_\nu}{\partial\alpha(nl)\,\partial\alpha(n'l')}\;.\end{aligned} \tag{64}$$

We find that

$$\langle N_{(nl)} N_{(n'l')} \rangle_N = Q(nl, n'l') + \delta_{nn'} \delta_{ll'} [Q(nl, nl)/(4l+2) - q(nl)] , \quad (65)$$

and that the final results are

$$Q(3d, 4s) = q(3d)\, q(4s) + \frac{\partial q(3d)}{\partial \alpha(4s)} \quad (66)$$

and

$$Q(nl, nl) = \left[\frac{4l+2}{4l+1}\right] \left[q^2(nl) - q(nl) + \frac{\partial q(nl)}{\partial \alpha(nl)} \right] . \quad (67)$$

Slater's energy expressions are retrieved from these expressions when the second derivatives of the logarithm of the generating function are discarded but there seems to be no acceptable ensemble for which this is justified except for integer occupation numbers $q(3d)$ and $q(4s)$. The ensemble-average procedure used here for the calculation of $Q(nl, nl)$ leads always to positive values and ensures that $\langle H \rangle_N$ is an upper bound to the ground-state energy for the N-electron atom.

It can be made plausible that $\langle H \rangle$ is also an upper bound to the ground-state energy $E_0(N)$ for a fixed value of $N = \sum q(nl)$. For integer values of $q(nl)$ it follows readily that

$$E_0(N) \leq \langle H \rangle - \tfrac{1}{2} \sum q(nl) [4l + 2 - q(nl)] \times V(nl, nl)/(4l+1) ,$$

while $\langle H \rangle$ is greater for integer values of the $q(nl)$'s than for the optimal choice of them for a fixed N.

The explicit form of Z_ν is readily obtained as

$$Z_\nu = e^{\nu\alpha(3d)} \left[\binom{10}{\nu} + 2\binom{10}{\nu-1} e^{\alpha} + \binom{10}{\nu-2} e^{2\alpha} \right] , \quad (68)$$

with

$$\alpha = \alpha(4s) - \alpha(3d) . \quad (69)$$

The actual calculation of $q(nl)$ and $Q(nl, n'l')$ is conveniently done in complex arithmetic in the computer starting from the integration formula (61) which is easily generated. The form (68) shows that only for $|\alpha| \gg 1$ will one term dominate and thus second derivatives of $\ln Z_\nu$ be negligible. This happens for nearly full or nearly empty subshells.

The difference between Slater's energy expression and the form $\langle H \rangle_N$ is conveniently expressed in terms of $\partial q(4s)/\partial \alpha(4s)$ when we realize that relation (59) gives

$$\frac{\partial q(3d)}{\partial \alpha(4s)} = - \frac{\partial q(4s)}{\partial \alpha(4s)} \quad (70)$$

and

$$\frac{\partial q(3d)}{\partial \alpha(3d)} = - \frac{\partial q(4s)}{\partial \alpha(3d)} , \quad (71)$$

and the properties of second derivatives guarantee that

$$\frac{\partial q(4s)}{\partial \alpha(3d)} = \frac{\partial q(3d)}{\partial \alpha(4s)} . \quad (72)$$

We have in terms of interaction integrals $(nl, n'l')$ of Ref. 1 and Eq. (37) that the hyper-Hartree-Fock (HHF) total energy formula is

$$E(\mathrm{HHF}) = \langle H \rangle_N - [(4s, 4s) - 2(3d, 4s) + (3d, 3d)] \frac{\partial q(4s)}{\partial \alpha(4s)} . \quad (73)$$

The derivative is positive and its coefficient turns out to be positive and E(HHF) will generally be lower than the variational bound $\langle H \rangle_N$ of Eq. (39).

IV. RESULTS

The calculations that we present in this section were performed for a set of varying occupation numbers for the 4s and 3d orbitals. We give in Fig. 1 a display of the variation of the orbital energies $\epsilon(3d) = \partial\langle H \rangle/\partial q(3d)$ and $\epsilon(4s) = \partial\langle H \rangle/\partial q(4s)$ as functions of $q(3d)$ for a few fixed values of $q(4s)$ and for the nuclear charge of Fe. This shows the monotonic increase in orbital energies as the number of electrons in the 3d subshell increases. The orbital energy $\epsilon(4s)$ is always larger than the corresponding $\epsilon(3d)$. A similar display occurs in Fig. 2 but here the sum of the occupation numbers $q(4s)$ and $q(3d)$ is kept constant and equal to 8, the number of valence-shell electrons in iron.

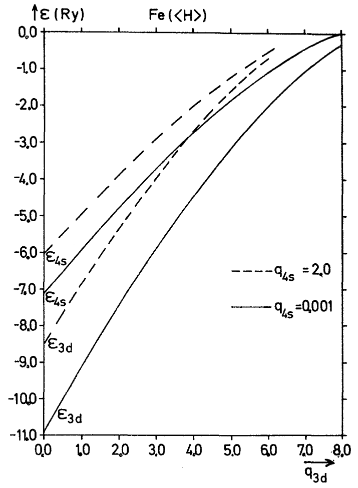

FIG. 1. Orbital energies in Ry for the valence shells in Fe ions as a function of the number of 3d electrons found by the energy functional $\langle H \rangle$. Full line means that the 4s shell is almost empty ($q_{4s} = 0.001$) and dotted line that the 4s shell is full ($q_{4s} = 2$).

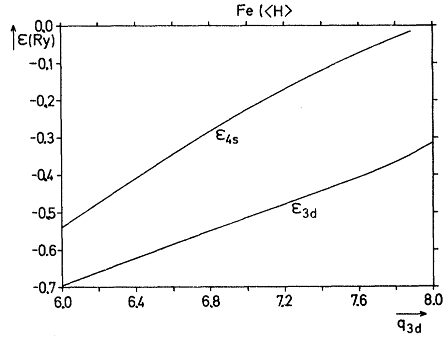

FIG. 2. Orbital energies in Ry for the valence shells in neutral Fe as a function of the number of 3*d* electrons found by the energy functional $\langle H\rangle$.

Again we see that $\epsilon(4s)$ lies above $\epsilon(3d)$ and that both are increasing functions of $q(3d)$.

The present calculations can be compared to the results of the hyper-Hartree-Fock method and we list in Tables I and II orbital energies obtained by several different arguments. The differences are relatively small for inner-shell energies. It is seen that the modified orbital energies E' defined in Ref. 1 do not compare well with $\partial\langle H\rangle/\partial q$. This reflects the difficulty in the generalization of the hyper-Hartree-Fock energy functional to continuously varying occupation numbers. Total energies as functions of occupation number $q(3d)$ are given in Fig. 3 for atomic Fe and for Fe$^+$ as calculated from the functionals $\langle H\rangle$ and $\langle H\rangle_N$. It holds that the minimum energy $\langle H\rangle$ is obtained when the 4*s* orbital is empty. The energy functional $\langle H\rangle_N$ attains its minimum for a full 4*s* subshell for Fe but has its smallest value for an empty 4*s* subshell for Fe$^+$.

In view of these results it is clear that a description of transition-metal states as simple configurations is ambiguous and that a more complete account has to be taken of the electron interaction terms in the Hamiltonian than what is possible in a central-field idea. A direct calculation of term energies for Fe, Fe$^+$, and Fe^{++} based on the orbitals that are optimal for the minimization of $\langle H\rangle$ gives the result that Fe^{++} has the ground-state configuration $3d^6$, that Fe$^+$ is described as $3d^6 4s$, and that Fe in the ground state is given as $3d^6 4s^2$. Thus it seems that the orbitals obtained from Eq. (45) are equally appropriate as starting functions for detailed calculations as are those calculated by traditional or hyper-Hartree-Fock methods. Minimum values of some energy functionals are given for comparison in Table III. The differences between the entries for a given configuration in Table III are mainly the effect of different coefficients for electron repulsion integrals and to a smaller extent from the fact that different entries are calculated with different orbitals.

TABLE I. Orbital energies obtained from variations of energy functionals for hyper-Hartree-Fock; derivative with respect to occupation number of hyper-Hartree-Fock (E'); projected ensemble and unprojected ensemble average for Ni $3d^8 4s^2$ in Ry.

	HHF	E'	$\langle H\rangle_N$	$\langle H\rangle$
$\epsilon(1s)$	−611.2537	−594.1117	−611.254	−611.448
$\epsilon(2s)$	−75.8529	−72.1913	−75.853	−76.056
$\epsilon(2p)$	−65.90006	−61.8391	−65.901	−66.102
$\epsilon(3s)$	−9.7871	−8.5838	−9.787	−9.912
$\epsilon(3p)$	−6.5661	−5.4605	−6.566	−6.683
$\epsilon(3d)$	−1.3942	−0.4516	−1.394	−1.106
$\epsilon(4s)$	−0.5536	−0.2567	−0.554	−0.565

V. EFFECTIVE INTERACTIONS IN VALENCE SHELL

We study more closely in this section the energy expression $\langle H\rangle$ from Eq. (38) with a view of using it as a starting point for a description of the multiplet structure in the valence shell and for a discussion of the implications for calculations on molecular and crystalline electronic structure. The average value $\langle H\rangle$ is appropriate for generating a model which may simulate the properties of an atom in terms of its valence-shell atomic orbitals since the average formation includes all possible states that can be obtained with the given set of orbitals.

The total energy $\langle H\rangle$ can be expanded in a Taylor series around a standard configuration specified through a set $[q_0(nl)]$. We define

$$\delta q(nl) = q(nl) - q_0(nl) \tag{74}$$

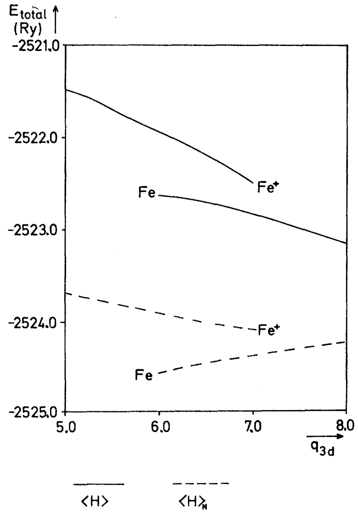

FIG. 3. Total energies in Ry for Fe and Fe$^+$ as a function of the number of 3*d* electrons. Full line means found by the energy functional $\langle H\rangle$ and dotted by $\langle H\rangle_N$.

TABLE II. Orbital energies in Ry for valence orbitals of Fe, Co, and Ni for different configurations found by different methods.

	E_{HHF} $3d$	E_{HHF} $4s$	E' $3d$	E' $4s$	$\langle H\rangle_N$ $3d$	$\langle H\rangle_N$ $4s$	$\langle H\rangle$ $3d$	$\langle H\rangle$ $4s$
Fe $3d^{6.0}4s^{2.0}$	−1.2157	−0.5203	−0.3769	−0.2407	−1.216	−0.520	−0.694	−0.544
Co $3d^{7.0}4s^{2.0}$	−1.3061	−0.5372	−0.4149	−0.2488	−1.306	−0.537	−0.894	−0.555
$3d^{7.2}4s^{1.8}$	−1.2094	−0.5204	−0.3303	−0.2378	−1.179	−0.536	−0.850	−0.484
$3d^{7.4}4s^{1.6}$	−1.1157	−0.5037	−0.2489	−0.2268	−1.066	−0.532	−0.806	−0.416
$3d^{7.5}4s^{1.5}$	−1.0700	−0.4953	−0.2095	−0.2214	−1.014	−0.530	−0.785	−0.383
$3d^{7.6}4s^{1.4}$	−1.0251	−0.4869	−0.1709	−0.2160	−0.965	−0.528	−0.763	−0.351
$3d^{7.8}4s^{1.2}$	−0.9379	−0.4701	−0.0965	−0.2053	−0.873	−0.525	−0.719	−0.288
$3d^{8.0}4s^{1.0}$	−0.8540	−0.4534	−0.0259	−0.1948	−0.790	−0.522	−0.675	−0.227
$3d^{8.5}4s^{0.5}$	−0.6610	−0.4116	−0.1325	−0.1694	−0.617	−0.526	−0.563	−0.092
$3d^{8.8}4s^{0.2}$	−0.5578	−0.3870	−0.2138	−0.1551	−0.537	−0.536	−0.488	−0.026
$3d^{9.0}$	−0.4948		−0.2616		−0.494		−0.416	
Ni $3d^{8.0}4s^{2.0}$	−1.3942	−0.5536	−0.4516	−0.2567	−1.394	−0.554	−1.106	−0.565
$3d^{8.2}4s^{1.8}$	−1.2931	−0.5361	−0.3622	−0.2451	−1.264	−0.552	−1.055	−0.492
$3d^{8.4}4s^{1.6}$	−1.1949	−0.5185	−0.2761	−0.2336	−1.148	−0.546	−1.004	−0.422
$3d^{8.5}4s^{1.5}$	−1.1469	−0.5097	−0.2342	−0.2279	−1.094	−0.544	−0.979	−0.388
$3d^{8.6}4s^{1.4}$	−1.0997	−0.5009	−0.1932	−0.2222	−1.043	−0.541	−0.953	−0.354
$3d^{8.8}4s^{1.2}$	−1.0077	−0.4832	−0.1138	−0.2109	−0.947	−0.536	−0.902	−0.289
$3d^{9.0}4s^{1.0}$	−0.9190	−0.4653	−0.0380	−0.1997	−0.859	−0.531	−0.850	−0.227
$3d^{9.5}4s^{0.5}$	−0.7131	−0.4203	−0.1341	−0.1723	−0.669	−0.535	−0.715	−0.089
$3d^{9.8}4s^{0.2}$	−0.6014	−0.3929	−0.2244	−0.1563	−0.580	−0.548	−0.623	−0.023
$3d^{10.0}$	−0.5324		−0.2786		−0.532		−0.532	

and obtain

$$\langle H\rangle = \langle H\rangle_0 + \sum \epsilon(nl)\,\delta q(nl) + \tfrac{1}{2}\sum V_{\mathrm{eff}}(nl, n'l')\,\delta q(nl)\,\delta q(n'l') + \cdots \tag{75}$$

with the notation

$$V_{\mathrm{eff}}(nl, n'l') = \frac{\partial^2\langle H\rangle}{\partial q(nl)\,\partial q(n'l')} = \frac{\partial\epsilon(nl)}{\partial q(n'l')} , \tag{76}$$

which anticipates the interpretation of the second derivatives as effective interaction integrals. Landau uses a similar expression in order to define an effective Hamiltonian for Fermi liquids.[11] Jørgensen has introduced the concept of differential ionization energy for an atom[12] as a function $I(z)$ of a continuous charge parameter z which is such that the n'th ionization energy I_n is given as

$$I_n = \int_{n-1}^{n} I(z)\,dz . \tag{77}$$

The function $I(z)$ is approximated as a polynomial with a few terms which are obtained by comparisons to experimental data. These results cannot directly be compared to the orbital energies $\epsilon(nl) = \partial\langle H\rangle/\partial q(nl)$ since $\langle H\rangle$ is an average over

TABLE III. Total energies in Ry for Cr, Fe⁺, Fe, Co, and Ni found by different methods.

	q_{4s}	0.5	1.0	1.5	2.0
Cr	$\langle H\rangle_N$	−2086.075	−2086.156	−2086.243	−2086.353
	$\langle H\rangle$	−2084.615	−2084.595	−2084.617	−2084.685
Fe⁺	$\langle H\rangle_N$	−2524.026	−2523.918	−2523.777	−2523.689
	$\langle H\rangle$	−2522.212	−2521.942	−2521.699	−2521.489
Fe	$\langle H\rangle_N$	−2524.316	−2524.392	−2524.474	−2524.582
	$\langle H\rangle$	−2522.994	−2522.842	−2522.716	−2522.608
Co	$\langle H\rangle_N$	−2762.361	−2762.434	−2762.511	−2762.617
	$\langle H\rangle$	−2761.406	−2761.175	−2760.961	−2760.775
	E_{HHF}	−2762.490 02	−2762.608 77	−2762.654 94	−2762.617 13
Ni	$\langle H\rangle_N$	−3013.387	−3013.464	−3013.532	−3013.632
	$\langle H\rangle$	−3013.041	−3012.727	−3012.422	−3012.139
	E_{HHF}	−3013.523 80	−3013.641 87	−3013.681 57	−3013.631 90

state energies for many different degrees of ionization. An analysis can be made which permits us to calculate theoretical parameters of $I(z)$ from the orbital energy of the $3d$ level for some transition metals and to compare these with the ones derived by Jørgensen. The energy of a configuration with N electrons in the $3d$ subshell will be denoted $E(N)$. The definition (77) then leads to the relation that

$$E(N-\nu)=E(N)+\int_0^{\nu} I(z)\,dz \ . \tag{78}$$

We put

$$I(z)=a_0+a_1 z+a_2 z^2+\cdots \tag{79}$$

and obtain for the average energy

$$\langle H\rangle=\sum_\nu w_\nu E(N-\nu)$$
$$=E(N)+a_0\langle\nu\rangle+\tfrac{1}{2}a_1\langle\nu^2\rangle+\tfrac{1}{3}a_2\langle\nu^3\rangle+\cdots \ , \tag{80}$$

where we can identify the formal charge z of the atom as $\langle\nu\rangle$. We find that for an ensemble of the type (15) for one open subshell it holds that

$$\langle\nu\rangle=z \ ,$$
$$\langle\nu^2\rangle=z^2+(N-z)(4l+2+z-N)/(4l+2) \ , \tag{81}$$
$$\langle\nu^3\rangle=z^3+(N-z)(4l+2+z-N)$$
$$\times[3z(2l+1)+N-z-2l-1]/(4l+2)(2l+1) \ .$$

The orbital energy $\epsilon(nl)$ can now be calculated as

$$\epsilon(nl)=-\partial\langle H\rangle/\partial z=\tilde{a}_0+\tilde{a}_1 z+\tilde{a}_2 z^2+\cdots \tag{82}$$

and a comparison between a polynomial fit to the calculated orbital energies and the derivation from Jørgensen's parameters is made in Table IV.

The coefficient $\tilde{a}_1$ corresponds to the $V_{\text{eff}}(nl,nl)$ for the valence subshell and we see in Table V a comparison between these parameters and the integrals $V(nl,nl)$. It is clear that a considerable modification results in going from V to V_{eff} and this is a reflection of the adjustment of the orbital form upon change of occupation numbers $q(nl)$. A large amount of screening of the electron interaction is thus accounted for and the effective interaction parameters may be used instead of the integrals calculated directly from the orbitals in a description of the multiplet structure in a central-field model. There does not seem to be a corresponding procedure for the separate evaluation of the F^k and G^k integrals.

TABLE IV. Comparison of differential ionization energies in Ry from calculational and experimental data.

	Fe	Co	Ni
$\tilde{a}_0$ (calc)	0.314	0.416	0.532
$\tilde{a}_0$ (expt)	0.211	0.635	1.117
$\tilde{a}_1$ (calc)	0.581	0.668	0.751
$\tilde{a}_1$ (expt)	0.925	0.976	1.026
$\tilde{a}_2$ (calc)	0.177	0.166	0.151
$\tilde{a}_2$ (expt)	0.059	0.066	0.072

TABLE V. Comparison of calculated and experimentally derived effective interaction parameters $V_{\text{eff}}(3d,3d)$ and unmodified parameters $V(3d,\ 3d)$ in Ry.

	Fe	Co	Ni
V_{eff} (calc)	0.581	0.668	0.751
V_{eff} (expt)	0.955	0.976	1.026
V	1.219	1.342	1.460

Jørgensen noted that the coefficient a_0 is approximately equal to the electronegativity of the atom according to the definition by Mulliken[13]:

$$X=\tfrac{1}{2}(I_0+I_1)=a_0+\tfrac{1}{3}a_2+\cdots \ . \tag{83}$$

It is thus a close resemblance between the electronegativity parameter X and the calculated orbital energy $\epsilon(nl)$. The derivative relation (51) indicates that a chemical potential for an atom may be defined as the negative of the electronegativity parameter X, which only is a confirmation of the concept of electronegativity as being the power of accepting electrons.

A model for an atom may now be constructed as having basis orbitals from the valence shell with matrix elements computed from $\epsilon(nl)$ and $V_{\text{eff}}(nl,n'l')$ rather than from $I(nl)$ and $V(nl,n'l')$. Such a model is similar to conventional ones where empirical values for integrals are used, and offers a well defined functional form of the orbitals, which may be used for the calculation of overlap integrals and other multicenter integrals which are used in a theory of molecular electronic structure. We are in the process of exploring these possibilities.

VI. CONCLUSIONS

Two alternatives to the hyper-Hartree-Fock method for atoms with open shells have been discussed here. Both alternatives are derived employing ensemble averages, and they allow fractional occupation numbers in the subshells. The total energy for a fixed value of $N=\sum q(nl)$ is an upper bound to the ground-state energy in one case ($\langle H\rangle_N$) and probably is such a bound in the other case as well ($\langle H\rangle$).

The procedure, employing the functional $\langle H\rangle$, admits consideration of noninteger total number of electrons in the system in the sense that the average formation involves states with varying degrees of ionization. This method is formally related to the Hartree-Fock method for extended systems using temperature-dependent averages.

The numerical results of the three methods are not very much different for inner-shell orbital energies, total energies, and wave functions. There is a distinct difference in the description of the ground-state configuration obtained from the three methods applied to transition metals. The energy average $\langle H\rangle_N$ has its minimum for the configuration $3d^q 4s^2$ for the four atoms Cr, Fe, Co, and Ni that have been studied here, while the average $\langle H\rangle$ has its minimum for $3d^{q+2}$, and the hyper-Hartree-Fock method points towards an intermediate situation. We feel that wave functions obtained from Eq. (45) and the corresponding potential functions are those best suited for molecular or solid-state applications since the treatment of Coulomb and exchange terms is here similar to the ones used in a tight-binding formulation of the Hartree-Fock method for a molecule or crystal. The valence-shell orbitals are in this case somewhat more diffuse than those obtained by the other procedures and it is necessary to subject this point to a careful analysis with regard to possible "overlap catastrophies."

The connection between the electronegativity concept and the valence-shell orbital energy as defined by Eq. (51) is a satisfying feature of the Hartree-Fock procedure based on ensemble averages without restriction to fixed number of electrons. A further study of the significance of this relation for the discussion of chemical bonding and molecular electronic structure is needed.

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[1] J. C. Slater, J. B. Mann, T. M. Wilson, and J. H. Wood, Phys. Rev. 184, 672 (1969).

[2] See, e.g., E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge, U. P., Cambridge, England, 1953), p. 335.

[3] J. C. Slater, Phys. Rev. 34, 1293 (1929).

[4] D. R. Hartree, Proc. Cambridge Phil. Soc. 24, 89 (1928).

[5] R. K. Nesbet, Proc. Roy. Soc. (London) A230, 312 (1955); Rev. Mod. Phys. 33, 28 (1961).

[6] L. Brillouin, Actualites Sci. Ind. 71, 1 (1933).

[7] J. C. Slater, Intern. J. Quantum Chem. 3S, 727 (1970).

[8] W. Moffitt, Proc. Roy. Soc. (London) A210, 245 (1951).

[9] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Vol. I., p. 217.

[10] T. Koopmans, Physica 1, 104 (1933).

[11] L. D. Landau, Zh. Eksperim. i Teor. Fiz. 30, 1058 (1956); 32, 59 (1957) [Sov. Phys. JETP 3, 920 (1956); 5, 102 (1957)].

[12] C. K. Jørgensen, *Orbitals in Atoms and Molecules* (Academic, London, 1962), p. 85.

[13] R. S. Mulliken, J. Chem. Phys. 2, 782 (1934).

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Molecular-Beam Magnetic-Resonance Measurements of the Anisotropies of the Electric Polarizabilities of H_2 and D_2[†]

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The anisotropies $\gamma = \alpha_{\parallel} - \alpha_{\perp}$ of the static electric polarizabilities of H_2 and D_2 were measured in a molecular-beam magnetic-resonance experiment. The quadratic Stark shifts of the separated-oscillatory-field resonances in the ground electronic and vibrational and $J = 1$ rotational states were measured in parallel electric and magnetic fields. The results are $\gamma(H_2) = 0.3016 \pm .0005$ Å^3 and $\gamma(D_2) = 0.2917 \pm .0004$ Å^3, which agree very closely with theory. A previously measured combination of the spin-rotation and quadrupole-interaction constants of D_2 was independently remeasured, and the dependence upon orientation of the nuclear magnetic shielding of D_2 was found to be $\sigma_{\pm 1} - \sigma_0 = -11 \pm 9$ ppm. An efficient electron-bombardment detector was constructed for this experiment.

I. INTRODUCTION

We report here the first direct measurement of the anisotropy of the static polarizability of H_2 and an improved measurement for D_2, each in the ground electronic and vibrational state and the $J = 1$ rotational state. The method is basically that used by English and MacAdam,[1] namely, the measure-