Local Exchange Approximation and the Virial Theorem*†

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(Received 14 March 1969)

Whereas the determinantal wave functions constructed from the solutions of the Hartree-Fock equations satisfy the virial theorem, those constructed from self-consistent-field schemes with a local exchange approximation do not necessarily. A scaling procedure, which goes back to Fock, allows considerable improvement and good agreement with the Hartree-Fock results. The virial theorem criterion agrees with previous empirically based assertions that Slater's potential "overestimates" exchange effects. In addition, and also in an *ab initio* way, it can be added that Kohn and Sham's potential "underestimates" them, at least for light atoms. Numerical results and comparison of various methods are presented. A Slater-type local exchange potential is suggested, $V_{HFS}'' = -X6[(\frac{3}{8}\pi)\rho(\vec{r})]^{1/3}$, where X is determined by the virial theorem. Applications to solid-state physics are discussed.

I. INTRODUCTION

The Hartree-Fock (HF) equations have been the cornerstone upon which most of atomic, molecular, and solid-state theory has been built. Some of the applications required approximations, and those proposed by Slater proved to be extremely fruitful.[1] He suggested replacing the nonlocal exchange terms in the original equations by an averaged local exchange potential. He further approximated this average by the exchange potential of a free-electron gas with the same local density. That is,

$$V_{exc}\varphi_i(\vec{r}) = -\sum_j \int \varphi_j^*(\vec{r}')\varphi_i(\vec{r}')\frac{2}{|\vec{r}-\vec{r}'|}d^3r'$$

$$\times \varphi_j(\vec{r})\delta_{m_{s_i} m_{s_j}} \qquad (1)$$

is replaced by

$$V_{HFS}\varphi_i(\vec{r}) = -6[(\tfrac{3}{8}\pi)\rho(\vec{r})]^{1/3}\varphi_i(\vec{r}), \qquad (2)$$

where $\rho(\vec{r})$ is the electron density.

The Hartree-Fock-Slater (HFS) equations lead to a great number of useful calculations especially in connection with the augmented plane wave (APW) method for solids.[2] Several authors[3-5] proposed a modified exchange potential V_{HFS}' which is two-thirds of V_{HFS}, i.e., $V_{HFS}' = \frac{2}{3}V_{HFS}$. Computations with this modified potential (HFS') have been made and they seem to yield better comparison with HF in atomic calculations[5] and with experimental results for energy bands in solids.[6] From a fundamental point of view, it is not quite clear yet which one is to be preferred.[7]

In any case, it should be observed that whereas the wave functions provided by the HF method satisfy the virial theorem,[8,9] the HFS and HFS' ones do not necessarily. Yet, they can be ad-

justed so as to verify it by means of a scaling procedure.[9]

In this paper we study the effects of scaling, in both the HFS and HFS' schemes, upon a series of light atoms. The total and "binding" energies of electrons, as well as other properties are compared with the HF values. The improvements and the regularities observed are substantial. Moreover, comparison with more elaborate local exchange potentials,[10] is favorable to the scaled Slater-type exchange potentials.[11]

In the light of the scaling procedure, a better local exchange potential is proposed. It is Slater-type and the coefficient A is determined by the virial theorem. Applications are discussed, in particular to solid-state problems. It does not seem unreasonable that the coefficient determined for the atomic case could be carried over to the solid.

II. SCALING, THE VIRIAL THEOREM, AND LOCAL EXCHANGE

The reason why the HF wave function satisfies the virial theorem is simple. The expectation value of the Hamiltonian with respect to the HF function is stationary for arbitrary variations of the spin-orbitals, in particular for a norm-preserving scale transformation

$$\varphi(\vec{r}_1, \vec{r}_2, \dots, \varphi\vec{r}_N)$$

$$\to \varphi\eta \equiv \eta^{3N/2}\varphi(\eta\vec{r}_1, \eta\vec{r}_2, \dots, \eta\vec{r}_N). \qquad (3)$$

Thus, the HF determinant has optimum scale automatically, and from the early work of Fock[8] we know that any approximate function with this property verifies the virial theorem

$$\langle T_{op}\rangle = -\tfrac{1}{2}\langle V_{op}\rangle. \qquad (4)$$

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T_{op} and V_{op} stand for the total kinetic- and potential-energy operators, respectively. We consider here the atomic case, but there is no difficulty in generalizing to the molecular case. [8,9]

The HFS wave function does not necessarily satisfy (4), since the use of (2) instead of (1) does not prescribe any longer a total wave function which is stationary under arbitrary variations of the spin orbitals. The same applies to the HFS' scheme, even though it might be considered as derived from a variational procedure. [3,4]

The virial theorem expresses a balance between kinetic and potential energies. Any change of one of them should involve a concomitant change of the other. This imposes a necessary condition for approximate wave functions. Löwdin[9] has given a simple procedure for scaling an approximate solution to the Schrödinger equation. Since T_{op} and V_{op} are homogeneous, of degree -2 and -1, respectively, their expectation values with respect to a function with scale factor η can be expressed in terms of those with respect to the unscaled function:

$$T(\eta) \equiv \int \varphi_\eta^* T_{op} \varphi_\eta \, dv = \eta^2 T(1),$$

$$(5)$$

$$V(\eta) \equiv \int \varphi_\eta^* V_{op} \varphi_\eta \, dv = \eta V(1).$$

The total energy, which depends on η,

$$E(\eta) = \eta^2 T(1) + \eta V(1), \qquad (6)$$

is minimized by $\eta = \bar{\eta}$, where

$$\bar{\eta} = - V(1)/2T(1), \qquad (7)$$

and then the scaled function $\varphi_{\bar{\eta}}$ satisfies the virial theorem. [8,9] The optimal energy depends exclusively on the kinetic and potential energies of the unscaled functions. Obviously, any homogeneous operator Ω_{op} of degree p, has the scaled value

$$\Omega(\bar{\eta}) = \bar{\eta}^{-p} \Omega(1). \qquad (8)$$

This last relation shows that scaling affects the computation of physical quantities from an approximate wave function. The "stretching" or "shrinking" of (3) must be prescribed in a non-arbitrary fashion, given by (7).

In the case of the HFS and HFS' schemes for atoms there is no basic difficulty in computing $\bar{\eta}$. Once it has been determined, the scaled functions are given by (3) and for most applications the use of (8) will be a sufficient tool. The question is now how much does $\bar{\eta}$ differ from unity, and how significant is this difference in the numerical applications.

III. NUMERICAL RESULTS

We study the scale factors and total energies for light atoms in the nonrelativistic HFS and

HFS' schemes. The HFS and HFS' equations were solved, and the expectation values of the kinetic- and potential-energy operators obtained from the solutions led to the optimal scale factors and energies. Since we are dealing with approximations to the HF equations, we compare our results with the numerical HF values given by Froese[12] and the analytical ones of Clementi. [13]

The computer programs[14] were based on the work by Herman and Skillman[15] and by Zare. [16] In Table I we present the results for the unscaled HFS method and the scaled one (HFS-SC). In Table II the corresponding results are shown for the HFS' and HFS'-SC methods, i.e., unscaled and scaled local exchange approximations with exchange potential $V_{HFS'} = \frac{2}{3} V_{HFS}$.

The scale factors show remarkable regularity: In the HFS scheme they are always smaller than unity, and they are larger than unity in the HFS' method. They both approach one with increasing Z, yet for $Z = 36$ their difference with unity is still significant. This accounts for changes in the total energy and other properties which are non-negligible. The fact that the scale factors show these regularities is rather important. It has been stated that the HFS scheme "overestimates" exchange effects. [6] The results of Tables I and II indicate that, in this language the HFS' scheme "underestimates" them. More precisely, the virial theorem criterion indicates that the HFS wave functions should be "stretched" and the HFS' ones "shrunk." One may surmise that there exists a Slater-type potential such that the optimal scale factor associated to it is unity. For this potential the determinantal wave function automatically satisfies the virial theorem. Of course, A will not be a universal coefficient, but it will depend on the nuclear charge and configuration considered. We study this further in the discussion.

We see in Tables I and II that the HFS results improve more by scaling than the HFS' ones. Very roughly from 70 to 30% of the difference between the HF and HFS total energies is recovered by scaling in the range of Z from 3 to 36. In the same range, the HFS' energies improve approximately 0.005 Ry by scaling. The HFS' method agrees better with HF than HFS when we consider total energies before and after scaling, except in He and Li, where the HFS-SC results are better than the HFS'-SC ones.

With increasing Z both approximations, HFS and HFS', give smaller relative errors, before and after scaling. A reasonable question is how small can this error be for a given Z. Approaching this problem Lindgren[10] tried a local exchange potential of the form

$$V_{HFL} = - C6(\tfrac{3}{4}\pi^2)^{1/3} r^{1-m/3} u(r)^{m/3}, \qquad (9)$$

TABLE I. Energies and scale factors for some light atoms in the HFS scheme. The differences with HF value are denoted by Δ (HFS) and by Δ (HFS-SC) for the unscaled and scaled case, respectively. All values in Rydbergs.

Atom	$E(\text{HF})$[a]	$E(\text{HFS})$[b]	$E(\text{HFS-SC})$[c]	Δ (HFS)[d]	Δ (HFS-SC)[e]	$\bar\eta$[f]
He	$-5.723\,37$	-5.7071	-5.7229	0.0162	0.0005	$0.950\,14$
Li	-14.8655	-14.8460	-14.8628	0.0194	0.0027	$0.967\,53$
Be	-29.1461	-29.1123	-29.1349	0.0238	0.0112	$0.972\,89$
B	-49.0583	-49.0127	-49.0401	0.045_6	0.0182	$0.976\,90$
F	-198.8191	-198.690_8	-198.756_2	0.128_3	0.062_9	$0.982\,18$
Ne	-257.0948	-256.939_4	-257.018_6	0.155_4	0.076_2	$0.982\,75$
Na	-323.7198	-323.553_4	-323.637_3	0.166_4	0.082_5	$0.984\,16$
Mg	-399.2304	-399.048_2	-399.138_6	0.182_2	0.091_8	$0.985\,18$
Al	-483.7550	-483.562_0	-483.657_6	0.193_0	0.097_4	$0.986\,14$
Cl	-918.9662	-918.706_4	-918.829_2	0.259_8	0.1370	$0.988\,57$
Ar	-1053.6370	-1053.35_8	-1053.48_9	0.27_9	0.14_8	$0.988\,98$
K	-1198.3304	-1198.04_3	-1198.17_8	0.28_7	0.15_2	$0.989\,48$
Ca	-1353.520	-1353.21_3	-1353.35_4	0.30_7	0.16_6	$0.989\,89$
Kr	-5504.114	-5503.48_0	-5503.76_1	0.63_4	0.45_3	$0.992\,91$

[a]Reference 12.
[b]Total energy computed with the HFS wave function.
[c]Scaled total energy, computed with formulas (5)–(7).

[d]Δ (HFS) $= E(\text{HFS}) - E(\text{HF})$.
[e]Δ (HFS-SC) $= E(\text{HFS-SC}) - E(\text{HF})$.
[f]$\bar\eta$ is given by Eq. (7).

TABLE II. Energies and scale factors for some light atoms in the HFS′ scheme. The differences with the HF values are denoted by Δ (HFS′) and Δ (HFS′-SC) for the unscaled and scaled case, respectively. All values are in Rydbergs.

Atom	$E(\text{HF})$[a]	$E(\text{HFS}')$[b]	$E(\text{HFS}'\text{-SC})$[c]	Δ (HFS′)[d]	Δ (HFS′ -SC)[e]	$\bar\eta$[f]
He	$-5.723\,37$	-5.7157	-5.7190	0.0177	0.0044	$1.024\,66$
Li	-14.8655	-14.8553	-14.8597	0.0102	0.0058	$1.017\,64$
Be	-29.1461	-29.1362	-29.1404	0.0099	0.0057	$1.012\,15$
B	-49.0583	-49.0430	-49.0477	0.0153	0.0106	$1.009\,82$
F	-198.8191	-198.785_8	-198.790_3	0.0333	0.028_8	$1.004\,77$
Ne	-257.0948	-257.054_8	-257.059_1	0.040_0	0.035_7	$1.004\,08$
Na	-323.7198	-323.681_0	-323.685_6	0.038_0	0.034_2	$1.003\,78$
Mg	-399.2304	-399.194_6	-399.199_3	0.035_8	0.031_1	$1.003\,42$
Al	-483.7550	-483.717_7	-483.722_5	0.037_3	0.032_5	$1.003\,17$
Cl	-918.9662	-918.918_0	-918.923_0	0.048_2	0.043_2	$1.002\,34$
Ar	-1053.6370	-1053.58_6	-1053.59_1	0.05_1	0.04_6	$1.002\,18$
K	-1198.3304	-1198.28_1	-1198.28_6	0.04_9	0.04_4	$1.002\,06$
Ca	-1353.520	-1353.46_8	-1353.47_3	0.05_2	0.04_7	$1.001\,90$
Kr	-5504.114	-5504.00_5	-5504.01_0	0.10_9	0.10_4	$1.000\,95$

[a]Reference 12.
[b]Total energy computed with the HFS′ wave function.
[c]Scaled total energy computed with formulas (5)–(7).

[d]Δ (HFS′) $= E(\text{HFS}') - E(\text{HF})$.
[e]Δ (HFS′-SC) $= E(\text{HFS}'\text{-SC}) - E(\text{HF})$.
[f]$\bar\eta$ is given by Eq. (7).

where u is the *radial* electron density and C, n, and m are adjustable parameters (equal to unity in V_{HFS}). The minimum of the energy surface $E_{\text{HFL}}(C, n, m)$ determines the optimal values of C, n, and m. The freedom of adjustable parameters, involves the need to solve the self-consistent problem for each set (C, n, m). But there is a unique η associated to any Slater-type exchange potential, and in each case the self-consistent equations have to be solved only once. It is interesting to compare the simple scaling method with

Lindgren's more elaborate scheme, which gives very good results, but it is not, as claimed,[10] the best central local exchange potential approximation (energy-wise) to the HF solution.

In Table III we present the total energy and scale factors for argon obtained with various methods. It should be noted that some local exchange schemes involve a "tail" correction to account for a proper asymptotic behavior of the potential at large r.[15,17] The calculations reported in Tables I and II did not involve this "tail" correction

TABLE III. Total energies of argon obtained with different approximations to the HF equations. All values in Rydbergs.

Method	Energy	Difference from HF
HFS[a]	-1053.35_8	0.278
HFS-SC[a]	-1053.48_9	0.147
HFS-M[a]	-1053.38_0	0.256
HFS-MSC[a]	-1053.50_6	0.130
HFS'[a]	-1053.58_6	0.050
HFS'-SC[a]	-1053.59_1	0.045
HFS'-M[a]	-1053.53_9	0.097
HFS'-MSC[a]	-1053.54_6	0.090
HFL (Ref. 10)	-1053.586	0.050
HF (Ref. 11)	-1053.636	0.000

[a]Calculations with the technique described in this paper. HFS-M and HFS-MSC stand for the unscaled and scaled versions of the HFS method with the "tail" modification. Similarly for HFS'-M and HFS'MSC.

since it is not necessarily an improvement.[5] We tried it as a test in various cases because we could reproduce Lindgren's reported values for HFS and HFS' only when the "tail" correction was made. Calculations including the "tail" modification are denoted by HFS-M and HFS'-M.

Our results for argon, shown in Table III, as well as for other atoms which we do not report here for economy, indicate that the "tail" correction improves the HFS result, but it makes the HFS' one worse, thus confirming Cowan *et al.* results.[5] (Their calculations for argon with HFS and HFS' method disagree slightly with ours, in the same way as their reported HF value differs from Clementi's.[13]) It is seen that with much less flexibility than Lindgren, we are able to achieve the same agreement with the HF values. In fact, the values reported show that the HFS'-SC scheme is slightly better than HFL in this case. This of course, is not true in general, and quite probably Lindgren's scheme improves without a "tail" correction. The remarkable thing is that simple scaling of the HFS' solution yields similar or better results than the "optimum" potential.

The improvement in total energy is probably not as important as the effect of scaling on other properties. The "binding energies" of electrons in a free atom or ion are defined as the energy necessary to remove the electrons to infinity. Within the HF scheme Koopmans's theorem leads to approximate these energies by the eigenvalues of the HF equations. This is no longer true in the HFS and HFS' schemes where the "binding energies" are not equal to the eigenvalues ϵ_i, but are given by

$$E_i = \langle \psi_i | - \nabla^2 - 2Z/r | \psi_i \rangle$$
$$+ 2\sum_j [\langle \psi_i \psi_j | 1/r_{12} | \psi_i \psi_j \rangle$$
$$- \langle \psi_i \psi_j | 1/r_{12} | \psi_j \psi_i \rangle], \tag{10}$$

if one assumes that the spin orbitals of the atom and the ion are the same. Here ψ_i denotes the spin orbital $\varphi_i(\vec{r})\alpha(\sigma)$ or $\varphi_i(\vec{r})\beta(\sigma)$.

The E_i are, of course, sensitive to the scheme employed and to scaling. It is interesting to compare the results obtained with various methods with the HF results. As an example we make a thorough comparison in Table IV for argon and sodium.

It is verified that the eigenvalues E_i do not provide in general good approximation and in particular it should be noted that the HFS' E_i are considerably worse than the HFS E_i, especially the outermost one. The results obtained with (10) are improved by scaling, the HFS E_i being more sensitive to it. The outermost eigenvalue in the HFS scheme is exceptional in the sense that it is closer to the HF result than the value computed with (10) using the unscaled functions.

On the other hand it is striking to compare the E_i obtained using HFS'-SC with Lindgren's and the HF eigenvalues. The maximum difference of the HFS'-SC binding energies with the HF eigenvalues is 0.3 eV in argon and 0.6 eV in sodium. We report only these two atoms as an illustration, but the agreement for other light atoms is similar, e.g., the maximum difference for krypton is 0.8 eV. These results seem to indicate that a Slater-type approximation can reproduce quite accurately not only the total energy, but also the HF excitation spectrum.

A good criterion by which to judge the improvement upon scaling of the HFS and HFS' functions is to study expectation values other than the energy. Properties like the diamagnetic susceptibility and the nuclear magnetic shielding are particularly interesting, since they are sensitive to the behavior of the wave function at large and short distances from the nucleus, respectively. They are given by[18]

$$\chi_d = -\tfrac{1}{6} N\alpha^2 a_0{}^3 \sum_i \langle (r_i)^2 \rangle, \tag{11}$$

and by[19]

$$\sigma = \tfrac{1}{3} \alpha^2 \sum_i \langle (r_i)^{-1} \rangle, \tag{12}$$

where N is Avogadro's number, α the fine structure constant, and a_0 the Bohr radius.

The "stretching" or "shrinking" of the wave function, given by (3), affects χ_d and σ, and this certainly ought to be determined by the virial theorem criterion.

TABLE IV. "Binding energies" for the electron shells in argon and sodium obtained with different approximations to the HF equations. All values in eV. (The starred values are those closest to the HF result).

	Method	$1s$	$2s$	$2p$	$3s$	$3p$
Ar	$HFS(\epsilon_i)^a$	3162.4	309.98	246.61	27.92	13.69
	HFS^b	3206.2	323.86	248.34	31.19	12.88
	$HFS\text{-}SC^b$	3216.9	327.8	252.9	32.14	13.74
	$HFS'(\epsilon_i)^a$	3094.1	291.9	227.9	22.64	9.07
	HFS'^b	3229.2	335.9	261.4	35.16	16.4
	$HFS'\text{-}SC^b$	3227.2*	335.2*	260.6*	34.99*	16.3*
	HFL^c	3225.9	334.0	259.3	34.6	15.9
	$HF(\epsilon_i)^d$	3227.5	335.3	260.4	34.8	16.1
Na	$HFS(\epsilon_i)^a$	1061.5	63.6	34.2	3.2	
	HFS^b	1087.1	70.9	35.9	4.6	
	$HFS\text{-}SC^b$	1094.0	72.8	38.1	4.7	
	$HFS'(\epsilon_i)^a$	1024.3	54.6	27.3	2.0	
	HFS'^b	1103.4	77.1	42.4	5.0	
	$HFS'\text{-}SC^b$	1101.8*	76.6	41.9	4.98	
	HFL^c	1099.9	75.7*	41.0*	4.96*	
	$HF(\epsilon_i)^d$	1101.5	76.1	41.3	4.96	

[a] ϵ_i indicates the eigenvalue of the HFS or HFS' equations.

[b] We report the "binding energies," computed with (10), for the scaled and unscaled orbitals in the HFS and HFS' schemes.

[c] Reference 10.

[d] Reference 11. We report the eigenvalues ϵ_i.

Hartree-Fock-Slater wave functions have been used recently by Saxena and Narasimhan[20] for computing χ_d and σ. Since they use the "tail" correction, their method is in our notation HFS-M. In Table V we show how their results for Ne, Ar, and Kr are affected by scaling. The improvement is again non-negligible. Of course, it should be pointed out that the figures of Table V depend strongly on what kind of local exchange approximation is used and better results are obtained with HFS'-SC. Since we are not interested here in making a detailed comparison of the different schemes but to point out the significance of scaling and of the virial theorem, we will just mention two points. Scaling does *not* improve the expectation values for helium, but this is a special case, since the local exchange potential should not be there at all. Secondly, perusal of a complete set of expectation values of powers of r for argon, given by Cowan et al.[5] in the HFS and HFS' approximations, shows that the difference with HF is substantially diminished after scaling.

IV. DISCUSSION

The preceding results indicate that when the necessary condition for approximate wave functions given by the virial theorem is used to determine the optimum scale factor, a substantial amount of the difference between the HFS and

HFS' approximations with the HF method is recovered. The optimal scale factors lead to the unambiguous statement, independently from any empirical considerations, that the HFS method "overestimates" exchange effects and that the HFS' scheme "underestimates" them.

Furthermore, the HFS'-SC method compares with HF just as well as HFL, the scheme pro-

TABLE V. Local exchange approximations and the computation of physical properties. The effects of scaling on computed diamagnetic susceptibilities χ_d, Eq. (11), and nuclear magnetic shielding constants σ, Eq. (12).

	Atom	$HFS\text{-}M^a$	$HFS\text{-}MSC^b$	HF^c
χ_d	Ne	7.088	7.3218	7.429
	Ar	19.165	19.585	20.626
	Kr	29.058	29.470	31.315
σ	Ne	56.278	55.372	55.226
	Ar	125.40	124.05	123.76
	Kr	327.49	325.20	324.56

[a] Computations of Ref. 18, using the Hartree-Fock-Slater exchange with "tail" correction.

[b] Application of formula (8) to the previous results, using the appropriate $\bar{\eta}$ values.

[c] G. Malli and S. Fraga, Theoret. Chem. Acta 5, 275 284 (1966).

posed by Lindgren.[10] The latter does not retain the $\rho^{1/3}$ form of the exchange potential and introduces parameters which require the solution of the self-consistent equations several times before they converge to their optimal values. On the other hand, the HFS'-SC scheme has only one nonlinear parameter, immediately determined by (7), after the HFS' equations have been solved.

The question of which, V_{HFS} or V_{HFS}' should be preferred has been extensively discussed by Slater.[7] Anyhow, they both have the $\rho^{1/3}$ dependence, that is, they are what we call Slater-type local exchange potentials. If the coefficient A is determined by a variational ansatz like Kohn and Sham's,[4] it involves the use, for all electrons of the exchange potential correct only at the top of the Fermi distribution.[7] If, instead, the coefficient is chosen by averaging over the momentum of the electrons, the way Slater did, the resulting potential does not follow from a variational principle. From a fundamental point of view the latter may not be a drawback, as Slater has pointed out.

The empirical evidence in various fields does not indicate which should be preferred, since V_{HFS} "overestimates" exchange effects. Our results show that V_{HFS}' is not necessarily the best Slater-type potential to be used. Several applications, as computation of the electron density at the nuclear surface and alkali halide overlap integrals, would confirm this. These quantities are "extremely dependent on the amount of Slater exchange used."[21] In energy-band theory the experimentation with the correction represents a good part of the 5% of non-*ab initio* theory which goes into the augmented-plane-wave calculations.[22]

It might be desirable to have a nonempirical choice of the coefficient of $\rho^{1/3}$ such that the determinantal wave function associated to it automatically satisfies the virial theorem. This is accomplished by a potential $V_{HFS}'' = x V_{HFS}$, where x is chosen so that the optimal scale factor $\bar{\eta}$ is equal to unity. The wave function then has optimal extension in space. The coefficient x will depend on the ionic species considered and its configuration. It should not be difficult to determine it in the atomic case, since for each x, $\bar{\eta}$ is determined by (7).

An interesting consideration in this connection is that Slater's averaging over the momentum of the free electrons is retained in V_{HFS}''. Whereas V_{HFS} is associated with the average value of the function $F(\lambda)$ defined in Ref. 1, and V_{HFS}' is associated with $F(1)$, the potential V_{HFS}'' is connected with a "weighted" average of $F(\lambda)$ such that the virial theorem is satisfied for the determinantal wave function constructed from the solution of HFS''. Of course the weights cannot be specified at this stage; they are in a sense arbitrary, but are not needed at all from the practical point of view.

In Table VI we give some results obtained for the scheme HFS'', where $V_{HFS}'' = x V_{HFS}$ and

TABLE VI. Energies (in Rydbergs) and optimal scale factors obtained with different Slater-type local exchange approximations $V = - 6A [(\tfrac{3}{8}\pi) \rho(r)]^{1/3}$.

Atom	A	$\bar{\eta}$	E (unscaled)	E (scaled)
Li	1.0^a	0.967 53	14.8460	14.8628
	$2/3^b$	1.017 64	14.8553	14.8597
	$0.781 25^c$	1.000 02	14.8627	14.8627
	$0.875 00^d$	0.958 37	14.8605	14.8636
Na	1.0^a	0.984 16	323.553_4	323.637_3
	$\tfrac{2}{3}^b$	1.003 78	323.681_0	323.685_6
	$0.730 53^c$	1.000 01	323.689_7	323.689_7
	$0.734 37^d$	0.999 79	323.689_8	323.689_8
K	1.0^a	0.989 48	1198.04_3	1198.17_8
	$\tfrac{2}{3}^b$	1.002 06	1198.28_1	1198.28_6
	$0.721 19^c$	0.999 99	1198.28_7	1198.28_7
	$0.875 00^d$	1.001 27	1198.28_7	1198.28_9

[a] The value of A corresponds to the HFS scheme.

[b] The value of A corresponds to the HFS' scheme.

[c] This value of A corresponds to the HFS'' scheme; $A = x$, the coefficient for which $\bar{\eta} = 1.0$. Notice that the energy surface $E(A, \bar{\eta})$ does not have its minimum at $E(x, 1.0)$.

[d] This value of A is reported to show that the minimal energy is *not* associated to HFS'', even though we did not search for the actual minimum.

for which $\bar{\eta} = 1$. This scheme is an optimal compromise between simplicity and accuracy.

A point for further discussion is if this is going to be useful in band-theory calculations. The answer will be given by the practitioners of this field, but we venture that the affirmative answer is not entirely groundless.

The question of the choice of x in the solid-state case is immediate. Clearly, the optimal x for the solid could be determined only if an accurate cohesive energy calculation could be done. One could ask how much does x change when going from the separated ions to the solid, and how large are the errors made when the same x value is used. From the discussions of Fröman and Löwdin,[23] on the virial theorem and cohesive energies of solids, we should expect that very serious errors are not introduced. Their conclusion is that when one uses the same orbitals for the solid at the equilibrium distance as those employed for the free constituents, the cohesive energy is rather insensitive to scaling. What really is important is to have the virial theorem satisfied by the wave functions of the free ions to start with; then, proper account of the kinetic- and potential-energy changes in cohesion can be made. This is particularly true for ionic crystals.

Since cohesive energies for alkali halides from the APW method are already available,[24] it is interesting to see what is the best x for a solid. In a first approximation, according to the preceding arguments, it is desirable to have the virial theorem satisfied for the free ions. This is accomplished by the V_{HFS}'' scheme.

In summary, wave functions obtained from a local exchange approximation to the nonlocal Hartree-Fock exchange operator do not necessarily satisfy the virial theorem. Scaling improves the agreement with the HF scheme, and provides understanding of the properties of the Slater and the Kohn and Sham exchange. A Slater-type exchange potential leading to wave functions which satisfy the virial theorem is proposed.

ACKNOWLEDGMENTS

*Sponsored in part by the King Gustaf VI Adolf's 70 Years Fund for Swedish Culture, Knut and Alice Wallenberg's Foundation, and in part by the Air Force Office of Scientific Research through the European Office of Aerospace Research, United States Air Force under Contract No. AF 61(052)-874.

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Relativistic Treatment of the Shielding of the Electron and Proton Magnetic Dipole Moments in Atomic Hydrogen[†]

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(Received 17 March 1969)

The Breit equation for two Dirac particles in an external magnetic field, with anomalous magnetic moments introduced phenomenologically as Pauli moments, is taken as the starting point for a Chraplyvy-Barker-Glover reduction. First-order perturbation theory employing the nonrelativistic wave function for the ^2S ground state is then used to derive expressions for the diagonal matrix elements of the Hamiltonian which depend linearly upon the field. These expressions are symmetric in the masses and anomalous moments of the particles and agree with previous results to relative order α^2. However, additional higher-order terms arise due to changes in the anomalous moments (in principle, obtainable from field theory), to reduced mass corrections, and to factorization of the moments as free-particle moments times shielding corrections. Contributions to the shielding expressions are interpreted as arising from (1) relativistic mass corrections, (2) spin-orbit coupling, and (3) spin-other-orbit coupling. In the case of atomic hydrogen the first two effects dominate the electron shielding and the latter dominates the proton shielding. Similar calculations and interpretations may be applied to magnetic shielding in larger atomic and molecular systems.

I. INTRODUCTION

Because of the relative ease of performing theoretical calculations as well as experimental measurements on the bound electron-proton system, the hydrogen atom has long provided a fruitful testing ground for physical theories. In addition, new concepts which have arisen from successful theoretical treatments of interactions in atomic hydrogen have found useful application in discussing similar interactions in larger atomic and molecular systems. New precision measurements[1,2] of the electron-proton g-factor ratio in atomic hydrogen in its ground electronic state have made it of interest to reinvestigate the theory behind these measurements, since the experimental precision will soon be beyond that of presently available theoretical calculations.[2]

Both the electron and the proton g factors are modified when the two particles become bound to form the hydrogen atom. Calculation of bound-state modifications to the electron g factor, based on the Dirac equation for the electron in a central Coulomb field and an external magnetic field, have been performed.[3] Similarly, the modification of the proton g factor to order α^2 (α is the fine-structure constant) is the well-known Lamb

diamagnetic shielding correction.[4] The results of these calculations for the ^2S ground state are, to order α^2,

$$g_e(h) = 2(1 - \tfrac{1}{3}\alpha^2 Z^2),$$

$$g_p(h) = g_p(1 - \tfrac{1}{3}\alpha^2 Z), \tag{1}$$

where $g_e(h)$ and $g_p(h)$ are the electron and proton g factors for atomic hydrogen, g_p is the free proton g factor, and Z is the proton charge. These treatments may be extended[3,5] to higher order in α^2 (the next contributions, of order $\alpha^4 Z^4$ and $\alpha^4 Z^3$, are important for heavy atoms), but they then ignore important contributions discussed below. For example, it is commonly assumed that the Dirac result for the electron g factor $g_e = 2$ may be replaced in Eq. (1) by the more exact result obtained from quantum electrodynamics,[6]

$$g_e = 2[1 + \alpha/2\pi - 0.328\,\alpha^2/\pi^2 + O(\alpha^3)]. \tag{2}$$

This replacement is apparently a good approximation to order α^2, but not to order α^3, as is shown below. Furthermore, the above treatments neglect the effects of the motion of the proton, and they ignore the possibility of bound-state modifi-