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# Atomic Self-Consistent-Field Calculations Using Statistical Approximations for Exchange and Correlation*

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The $\rho^{1/3}$ approximation introduced by Slater for the exchange terms in the Hartree–Fock (HF) equations, with or without Latter's cutoff in the tail of the potential function, leads to serious errors when applied to excited configurations of atoms. A more accurate approximation (HX) is suggested in which Hartree's method is used for the self-interaction correction, and a modification of the Slater $\rho^{1/3}$ term is used to approximate the remainder of the HF exchange terms. The HX scheme is fairly simple; iterative convergence to self-consistent-field solutions is quite stable; and the resulting one-electron radial wave functions produce acceptably accurate values of one-electron and total binding energies, interaction parameters $F^k$, $G^k$, and $\zeta_i$, and expectation values of $r^n$. Perturbation-theory relativistic and correlation corrections are computed; the latter are based on the free-electron approximation, with empirical modifications to allow for differences between free and bound electrons. Results agree well with experimental ionization and excitation energies for a wide variety of configurations.

## I. INTRODUCTION

USING the Slater-Condon theory of atomic structure,[1,2] approximate, but still very useful, *ab initio* calculations can be made of atomic energy levels and spectra, either in the single-configuration approximation[3] or including configuration-interaction effects.[4] For this purpose, there are required theoretical values of: (1) the total binding energy of the spherically-averaged atom in each configuration of interest (corresponding to the center-of-gravity energy $E_{\mathrm{av}}$ of all possible states of the configuration); (2) the electrostatic and spin-orbit radial integrals $F^k$, $G^k$, and $\zeta_i$, in terms of which the energy splittings from $E_{\mathrm{av}}$ are expressible; (3) the more general Slater integrals $R^k$, if configuration-interaction effects are to be included; and (4) the dipole radial integrals for the transitions in question, if absolute transition probabilities are to be calculated.

All of these quantities are given by familiar expressions involving various integrals of the one-electron radial wave functions. In particular, using determinantal wave functions for the atom, the one-electron and total binding energies are given by[5]

$$E^i = E_k^i + E_n^i + \sum_{j\neq i} E^{ij} = (i|-\nabla^2|i) + (i|-2Z/r|i) + \sum_{j\neq i} E^{ij} \qquad (1)$$

and

$$E = \sum_i \Big(E_k^i + E_n^i + \sum_{j<i} E^{ij}\Big), \qquad (2)$$

where the Coulomb interaction energy $E^{ij}$ between electrons $i$ and $j$, averaged over all possible magnetic quantum numbers, is given by[2]

$$E^{nl,n'l'} = F^0(nl,n'l') - \tfrac{1}{2} \sum_k \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 G^k(nl,n'l') \qquad (3)$$

for nonequivalent electrons, and by

$$E^{nl,nl} = F^0(nl,nl) - \frac{(2l+1)}{(4l+1)} \sum_{k>0} \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}^2 F^k(nl,nl) \qquad (4)$$

for equivalent electrons.

The best wave functions to use for evaluating these quantities are ones obtained by solution of the Hartree-Fock (HF) equations for the spherically averaged atom. However, these equations are sufficiently complex that for certain types of excited configurations it may be difficult to obtain convergence to self-consistent solutions, even when fairly accurate initial estimates are available for the wave functions and eigenvalues.[6] Moreover, the approximations inherent in practical applications of the Slater-Condon theory are such[7] that radial wave functions of HF accuracy are not usually needed. Accordingly it seems worthwhile trying to find an approximate calculational method which will give wave functions of reasonable accuracy, and which at the same time is sufficiently simple to give results in a highly routine manner using only very rough starting information.

Perhaps the best known approximation to the HF

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[1] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, England, 1935), Sec. 4[5] and Chaps. 6 and 7.

[2] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Chaps. 12–14, 20–23.

[3] R. D. Cowan and N. J. Peacock, Astrophys. J. **142**, 390 (1965); **143**, 283 (1966); R. D. Cowan, J. Opt. Soc. Am. **56**, 1416A (1966); Astrophys. J. **147**, 377 (1967).

[4] R. N. Zare, J. Chem. Phys. **45**, 1966 (1966).

[5] In this paper, all equations and numerical results are for distances in Bohr units and energies in Ry (≅13.605 eV), except where explicitly stated otherwise.

[6] In the case of the comparatively simple configurations Ni II $3d^84d$ and Ga I $4s^24d$, considerable effort and computer time have failed to produce convergence at all with either of two distinctly different and normally satisfactory HF programs.

[7] B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (Interscience Publishers, Inc., New York, 1965), pp. 69–78.

TABLE I. Results for Ar I $3p^53d$, computed by various schemes.

| | | HFS | | HFSL | | | |
|---|---|---|---|---|---|---|---|
| | $H$ | $k_x=1.5$ | $k_x=1.0$ | $k_x=1.5$ | $k_x=1.0$ | HX | HF[a] |
| $E_k$(Ry) | 1038.266 | 1075.858 | 1048.054 | 1075.792 | 1047.997 | 1057.728 | 1052.670 |
| $E$(Ry) | −1052.527 | −1052.327 | −1052.614[b] | −1052.363 | −1052.622 | −1052.706 | −1052.664 |
| $\epsilon^{3s}$(Ry) | −2.527 | −2.504 | −2.262 | −2.583 | −2.288 | −2.892 | −3.162 |
| $E^{3s}$(Ry) | −3.464 | −2.679 | −3.132 | −2.759 | −3.157 | −3.139 | −3.162 |
| $\epsilon^{3p}$(Ry) | −1.440 | −1.430 | −1.228 | −1.507 | −1.252 | −1.781 | −1.831 |
| $E^{3p}$(Ry) | −2.075 | −1.381 | −1.801 | −1.456 | −1.823 | −1.812 | −1.831 |
| $\epsilon^{3d}$(Ry) | −0.113 | −0.039 | −0.023 | −0.136 | −0.120 | −0.118 | −0.117 |
| $E^{3d}$(Ry) | −0.117 | +0.008 | −0.107 | −0.041 | −0.116 | −0.117 | −0.117 |
| $\langle r^{-2}\rangle_{3p}$(a.u.) | 1.598 | 1.874 | 1.742 | 1.887 | 1.744 | 1.800 | 1.633 |
| $\langle r^{2}\rangle_{3p}$(a.u.) | 3.393 | 2.653 | 2.952 | 2.636 | 2.965 | 2.852 | 2.871 |
| $\langle r^{6}\rangle_{3p}$(a.u.) | 222.5 | 101.1 | 149.5 | 100.7 | 159.8 | 119.9 | 121.9 |
| $\langle r^{-2}\rangle_{3d}$(a.u.) | 0.018 | 0.198 | 0.060 | 0.140 | 0.041 | 0.030 | 0.027 |
| $\langle r^{2}\rangle_{3d}$(a.u.) | 118.5 | 44.60 | 115.6 | 53.28 | 94.15 | 99.81 | 104.11 |
| $\langle r^{6}\rangle_{3d}$(a.u.) | $6.6\times10^6$ | $1.5\times10^6$ | $13.1\times10^6$ | $1.3\times10^6$ | $4.1\times10^6$ | $4.6\times10^6$ | $5.0\times10^6$ |
| $F^0(3p,3d)$ (Ry) | 0.234 | 0.575 | 0.320 | 0.481 | 0.295 | 0.275 | 0.264 |
| $F^2(3p,3d)$ (Ry) | 0.020 | 0.193 | 0.064 | 0.137 | 0.044 | 0.033 | 0.029 |
| $G^1(3p,3d)$ (Ry) | 0.008 | 0.222 | 0.064 | 0.151 | 0.036 | 0.022 | 0.017 |
| $G^3(3p,3d)$ (Ry) | 0.004 | 0.129 | 0.036 | 0.087 | 0.020 | 0.012 | 0.010 |
| $\zeta_{3p}$(cm$^{-1}$) | 929 | 1169 | 1060 | 1179 | 1061 | 1089 | ... |
| $\zeta_{3d}$(cm$^{-1}$) | 0.1 | 11.4 | 2.4 | 7.6 | 1.2 | 0.5 | ... |

[a] See Ref. 22.

[b] If the total energy is not calculated from the quantum mechanical equations (1)–(4), but instead the exchange portion is computed with the aid of the statistical approximation, then $E_s=-1048.055$ Ry ($=-E_k$), in agreement with the virial theorem (6), which should apply in this case.

equations is the Hartree-Fock-Slater[8] (HFS) scheme, which consists of replacement of the HF exchange terms by the statistical potential-energy function

$$V_{xs}(r)=-k_x(24\rho/\pi)^{1/3} \tag{5}$$

derived from the exchange energy of a zero-temperature free-electron gas, $\rho$ here being the local electron density $\rho(r)$ in the atom. Slater chose the value $k_x=\frac{3}{2}$, so that the eigenvalue of the radial equation would have the physical significance of a one-electron binding energy, just as in the HF case (Koopmans's theorem).[9] For ground configurations this approximation is usually satisfactory. However, there is evidence[10–12] that better wave functions are obtained using the value $k_x=1$ derived from the variational principle[13,14] (and long used in the Thomas-Fermi-Dirac theory of the atom)[15]; the total kinetic and potential energy are then such as to satisfy the virial theorem

$$E_k=-\tfrac{1}{2}E_p=-E \tag{6}$$

(as do HF values), but the eigenvalues no longer represent one-electron binding energies. But regardless of the value used for $k_x$, the HFS approximation tends to be very poor for excited electrons because (for neutral atoms) the function (5) tends to zero at large radii instead of to the proper value $-2/r$ of the self-interaction portion of the exchange potential.[16] This results in much too small a magnitude for the eigenvalue $\epsilon^i$ of the excited electron, and a correspondingly poor wave function (see Table I).

The error in (5) has been partially corrected by Herman and Skillman[16] through use of a potential cutoff of the type suggested by Latter[17]: The total potential used in the one-electron radial equation is taken to be either that computed using (5) or the correct asymptotic value

$$\lim_{r\to\infty} V(r)=-2(Z-N+1)/r\,, \tag{7}$$

whichever is more negative. This modification [which we shall refer to as the Hartree-Fock-Slater-Latter (HFSL) method, though it is frequently referred to in the literature simply as HFS] insures that computed eigenvalues will never be less negative than the hydrogenic values, but they clearly will not be so negative as they would be if a gradual (rather than discontinuous) change were made to the limiting form (7). Moreover, this scheme may give very poor values of ionization energy when computed as the difference between total binding energies of atom and ion (which is the correct method in principle): Consider, for example, a configura-

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[8] J. C. Slater, Phys. Rev. **81**, 385 (1951), or Ref. 2, Appendix 22.

[9] T. Koopmans, Physica **1**, 104 (1934).

[10] D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957), p. 61.

[11] B. Y. Tong and L. J. Sham, Phys. Rev. **144**, 1 (1966).

[12] R. D. Cowan, A. C. Larson, D. Liberman, J. B. Mann, and J. Waber, Phys. Rev. **144**, 5 (1966).

[13] R. Gáspár, Acta Phys. Hung. **3**, 263 (1954).

[14] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[15] See, for example, P. Gombás, *Die Statistische Theorie des Atoms und ihre Anwendungen* (Springer-Verlag, Vienna, 1949), p. 78.

[16] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

[17] R. Latter, Phys. Rev. **99**, 510 (1955).

TABLE II. HFSL energies (Ry) for argon ($k_x=1.0$).

| Config. | $E$ | Ionization Energy $\Delta E$ | exp[a] |
|---|---|---|---|
| Ar I $3p^53d$ | $-1052.622$ | 0.150 | 0.1274 |
| Ar I $3p^54f$ | $-1052.572$ | 0.100 | 0.06277 |
| Ar I $3p^55g$ | $-1052.550$ | 0.078 | 0.04003 |
| Ar II $3p^5$ | $-1052.472$[b] | | |

[a] C. E. Moore, *Atomic Energy Levels* (U. S. National Bureau of Standards, Circular No. 467, U. S. Govt. Printing Office, Washington, D. C., 1949–1958), 3 vols; C. J. Humphreys, E. Paul, Jr., R. D. Cowan, and K. L. Andrew, J. Opt. Soc. Am., **57**, 855 (1967).

[b] Use of the HFS value $-1052.501$ Ry would give more accurate values of $\Delta E$ for the reason discussed in the text.

tion such as Ar I $3p^5nl$ with large $nl$, where the excited electron lies almost entirely outside the $3p^5$ core, and the potential-cutoff point therefore lies between core and outer electron. The excited electron sees the proper potential $-2/r$ almost everywhere, and this results in the proper hydrogenic wavefunction and eigenvalue. However, the potentials seen by the core electrons should be essentially identical in Ar I $3p^5nl$ and Ar II $3p^5$, but are in fact quite different because in the former case the potential is essentially a HFS one (the cutoff at $-2/r$ lying outside the core) whereas in the latter case the HFSL cutoff at $-4/r$ lies well within the core. The resulting difference in core energies for atom and ion greatly distorts the computed ionization energy, as illustrated in Table II.

It is true that for highly excited configurations the assumption made in Koopmans's theorem (that core wavefunctions are identical in atom and ion) is well satisfied so that the ionization energy can be obtained accurately simply by using the one-electron energy $E^i$ of the excited electron, but the ambiguities present in borderline cases make it clearly desirable to eliminate the error in $\Delta E$.

## II. HARTREE STATISTICAL-EXCHANGE SCHEME (HX)

The principal difficulty with the HFS method is that the Slater exchange term (5) provides a very poor approximation to the self-Coulomb-interaction correction, which at large $r$ forms the leading member of the exchange terms. The obvious solution is to go back to Hartree's original scheme and subtract out the self-interaction term exactly,[18] and then to use some sort of approximation only for the remaining portion of the Hartree-Fock exchange terms. Thus in the radial differential equation

$$[-d^2/dr^2+l_i(l_i+1)/r^2+V^i(r)]P_{n_il_i}(r)=\epsilon^iP_{n_il_i}(r)\,, \quad (8)$$

we shall use not the HFS potential

$$V(r)=-2Z/r+V_e(r)+V_{xs}(r) \quad (9)$$

[where $V_e$ is the classical electron-electron potential energy for the entire electron density $\rho(r)$], but rather

$$V^i(r)=-2Z/r+V_e'(r)+V_{xs}'(r)\,, \quad (10)$$

where $V_e'$ is the classical potential energy for the density $\rho-\rho^i$ of electrons other than $i$.

For $V_{xs}'$ we wish to find some reasonably simple analytical expression (based on the statistical approximation) which will approximate fairly closely the properties of the exact HF terms, among which may be included: (a) The function should vanish for any single-electron configuration, and for any two-electron configuration $ns^2$ (since exchange terms arise only between electrons of parallel spin); (b) the virial theorem (6) should be satisfied; (c) for each orbital, $\epsilon^i=E^i$; (d) radial wave functions for equal $l$ but different $n$ should be orthogonal. In addition to these internally-contained properties, we also wish the individual wave functions (as measured by the quantities $E^i$, $F^k$, $G^k$, $\zeta_i$, and $\langle r^n\rangle_i$) to agree as well as possible with the HF ones.

In order that requirement (a) be satisfied, we assume the desired expression to be a function of a modified electron density

$$\rho'(r)=\rho(r)-[\min(2,\omega_i)]\rho^i(r)\,, \quad (11)$$

where $\omega_i$ is the number of equivalent electrons $(n_il_i)^{\omega_i}$ in the configuration under consideration; that is, $\rho'$ is the total electron density less the densities of electron $i$ and of the electron (of same $nl$ but opposite spin) with which it is paired, if the latter exists.[19] One might then guess that $V_{xs}'$ could be obtained from $V_{xs}$ simply by replacing $\rho$ in (5) by $\rho'$; however, in order to provide greater flexibility, we consider the more general expression

$$-k_1(\rho'/\rho)^{k_0}(24\rho/\pi)^{1/3}\,, \quad (12)$$

of which the above guess constitutes the special case $k_1=k_x$, $k_0=\frac{1}{3}$. We have made calculations for a wide variety of atomic configurations using two different values of $k_0$, and have found empirically that properties (b) and (c) require $k_1\cong0.7$ with $k_0=1.0$, or $k_1\cong0.6$ with $k_0=\frac{1}{3}$. Detailed comparison of computed results $(E,E^i,\langle r^n\rangle,F^k,G^k)$ with the corresponding HF values[20–22] shows the case $k_0=1$ to be slightly better on the whole than $k_0=\frac{1}{3}$; the first case is also somewhat simpler (requiring computation of a cube root only once rather than for each orbital) and is the only one which will be considered further.

For most configurations, use of (12) gives acceptable agreement with HF results. However, a number of excited configurations have been encountered for which

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[18] C. A. Coulson and C. S. Sharma [Proc. Phys. Soc. (London) **79**, 920 (1962)] have used this approach rather than Latter's in correcting the Thomas-Fermi potential for self interaction.

[19] Another way of looking at the expression (11) is to note that the statistical exchange term is really a function of the density $\frac{1}{2}\rho$ of electrons having spin parallel to electron $i$; from $\frac{1}{2}\rho$ is to be subtracted $\rho^i$, unless there is only one electron in orbital $i$—in which case $\frac{1}{2}\rho$ contains only $\frac{1}{2}\rho^i$.

[20] C. Froese, J. Chem. Phys. **45**, 1417 (1966).

[21] J. M. Wilson (private communication).

[22] J. B. Mann, Jr. (private communication).

(12) is inadequate, the excited orbital appearing in some cases to require a decrease in the magnitude of (12) at large $r$, and in other cases to require an increase at small $r$. The latter is the more serious problem, and arises for an excited $d$ or $f$ electron in configurations such as Sc I $3d4s4d$, Cu I $3d^{10}4d$, Zn I $3d^{10}4s4d$, and Yb I $4f^{14}6s5f$. In these cases the value of $\epsilon^i$ for the outer electron may differ greatly from $E^i$, there are very serious departures from orthogonality [the overlap integral $(3d|4d)$ being as large as 0.4], and the wavefunction $P_i(r)$ may be more than an order of magnitude too large at small $r$—as shown both by comparison with HF, and by the fact that the computed $\zeta_i$ (which goes roughly as $\langle r^{-3}\rangle_i$) is much greater than experiment. These difficulties seem to result from a high sensitivity of the excited orbital to the depth of the inner potential well and to the height of the intermediate potential barrier which are formed (or tend to be formed) by the partial cancellation between the two terms of the effective potential $l(l+1)/r^2+V(r)$ in (8). We have found by trial and error that the difficulties can be removed by addition to (12) of a factor $f(r)$ which differs from unity only at small $r$ (i.e., in the vicinity of the inner well), and which is constructed as follows: The various orbitals $n_il_i$ of the configuration are to be arranged in the order of decreasing magnitude of binding energy (or eigenvalue). Then $f(r)\equiv 1$ for the $i$th orbital except in the two cases (a) $l_{i-1}=l_i\geqq 2$, or (b) $l_{i-2}=l_i\geqq 2$ and $\omega_{i-1}=1$. In either of these cases we take

$$\begin{aligned} f(r)&=1, && r\geqq r_0; \\ &=1+k_2(1-r/r_0), && r<r_0. \end{aligned} \qquad (13)$$

Here $r_0$ is the location of the $k$th node of the wave function $P_{n_il_i}$, where $k$ is the number of orbitals having $l=l_i$ and $n<n_i$. [If a double potential well exists, $k$ is also the number of antinodes lying in the inner potential well, so that the $k$th node is that which lies within the potential barrier; thus the effect of (13) is to modify the depth of the inner well.] It may be noted that the factor (13) serves a similar purpose to the off-diagonal energy parameters $\epsilon^{ij}$ which are required in the HF equations to produce orthogonality of wave functions of equal $l$.

As a final approximation to the non-self-interaction exchange terms we have taken

$$V_{x\bullet}'=-k_1f\left[\frac{\rho'}{\rho'+k_3/(n-l)}\right]\left(\frac{\rho'}{\rho}\right)\left(\frac{24\rho}{\pi}\right)^{1/3}, \qquad (14)$$

the quantity in brackets being included to provide improvement at large $r$ (small $\rho'$). Use of this approximation [with $k_1=k_2=0.7$, $k_3=0.5$] will be referred to as the Hartree-plus-statistical-exchange (HX) scheme.[23] Although the expressions (13) and (14) are moderately complicated, it is much simpler than the exact HF theory, gives results in reasonably good agreement with HF values in cases where the latter are available, and has routinely given results (in good agreement with experiment) for cases in which HF programs have converged only after repeated attempts, or have failed completely. All experience to date indicates that the HX scheme should give good results in the great majority of cases, and that if there do exist cases in which it will give unsatisfactory results, then these cases will give themselves away through poor agreement of $\epsilon^i$ with $E^i$ and/or poor orthogonality of wave functions of equal $l$, and can probably be handled by minor modification of the three arbitrary constants $k_1$, $k_2$, $k_3$.

## III. RELATIVISTIC AND CORRELATION CORRECTIONS

Before valid comparisons can be made between theoretical energies (either HX or HF) and experiment, account must be taken of relativistic and correlation effects; these we shall compute approximately via perturbation theory.

Although relativistic corrections to total binding energies become quite large for heavy elements, the main contributions come from the tightly bound inner electrons. Relativistic corrections to excitation and ionization energies of the outer electrons seldom amount to more than a few percent. Hence we need not calculate relativistic energies with high accuracy,[24,25] and will limit ourselves to the mass-velocity and Darwin corrections (as discussed, for example, by Herman and Skillman),[16] taking as relativistic correction to the total binding energy

$$E_r=\sum_i E_r^{\,i}=\sum_i (E_m^{\,i}+E_D^{\,i}), \qquad (15)$$

where

$$E_m^{\,i}=-\tfrac{1}{4}\alpha^2(i|[\epsilon^i-V^i(r)]^2|i) \qquad (16)$$

and

$$E_D^{\,i}=-\tfrac{1}{4}\alpha^2(i|[dV^i/dr][d/dr]|i), \qquad (17)$$

with $\alpha\cong 1/137$ the fine-structure constant.

The correlation energy [i.e., correlation effects over and above those resulting from the use of determinental wave functions, which are represented by the exchange terms in (1)–(4)] is of appreciable importance in the calculation of excitation and ionization energies, but is very difficult to compute accurately. We wish here to see what it may be possible to do with the aid of theoretical results on the correlation energy of a zero-temperature free-electron gas. This approach has been considered by numerous workers[11,14,26–28] and applied

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[23] The more descriptive abbreviation HSX has been avoided because the first two letters might be read as "Hartree-Slater" or "Herman-Skillman."

[24] C. W. Scherr, J. N. Silverman, and F. A. Matsen, Phys. Rev. **127**, 830 (1962).

[25] H. Hartmann and E. Clementi, Phys. Rev. **133**, A1295 (1964).

[26] P. Gombás, Acta Phys. Hung. **13**, 233 (1961).

[27] J. F. Barnes, Phys. Rev. **140**, A721 (1965), and references quoted therein.

[28] S. Lundqvist and C. W. Ufford, Phys. Rev. **139**, A1 (1965).

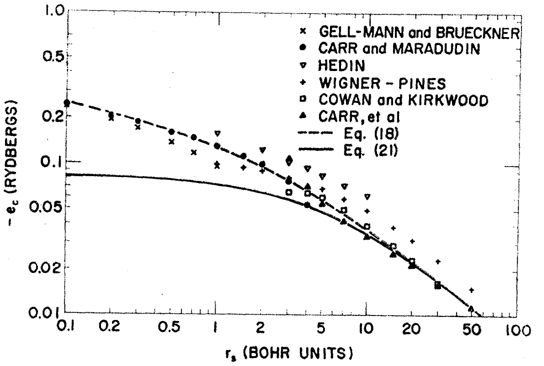

FIG. 1. The average correlation energy per electron in a zero-temperature, uniform free-electron gas. The plotted points are theoretical values calculated in various high- and low-density approximations, and the dashed line is the analytical fit of Eq. (18). The solid line represents the modified function of Eq. (21), suggested for use in calculating correlation energies of bound electrons in atoms.

to Thomas Fermi as well as self-consistent-field calculations.

Theoretical values of the average correlation energy per electron in a free-electron gas, calculated near the high-density[29–31] and low-density[32–34] limits are shown in Fig. 1 as a function of $r_s$, the radius of a sphere whose volume is the average volume per electron. The dashed curve is the function

$$e_c(r_s)=-\left[\frac{16.1}{1.54+\ln(r_s^{-1}+100)}+4r_s^{1/2}+1.142r_s\right]^{-1}, \quad (18)$$

which is an analytic fit to a rough graphical interpolation between the high- and low-density results.

Since $e_c$ represents the average energy per electron, the total correlation-energy correction for an atom is normally taken to be the volume integral

$$E_c=\int \rho e_c dv=4\pi\int_0^\infty \rho e_c r^2 dr, \quad (19)$$

where $\rho(r)$ is the total electron density and $e_c(r_s)$ is found as a function of $r$ from the definition $r_s=r_s(\rho)$. The correlation energy thus calculated from (18) and (19) is generally found to be considerably larger than that deduced from experiment.[11] One reason for this is that (19) includes self-correlation terms, being, for example, nonzero for a one-electron atom. The obvious indicated modification is to compute an energy $e_c^i=e_c(r_s^i)$ for an electron in orbital $i$ by using a value $r_s^i$ corresponding to the density $\rho-\rho^i$ of electrons other than $i$, and to use in place of (19)

$$E_c=\sum_i E_c^i, \quad E_c^i=4\pi\int_0^\infty \rho^i e_c^i r^2 dr. \quad (20)$$

[This refinement is unnecessary in the free-electron case, because each electron is spread throughout a large volume and the difference between $\rho$ and $\rho-\rho^i$ is infinitesimal.]

Even when the modified expression (20) is used, computed correlation corrections usually still prove to be too large. This may be due primarily to a second aspect of the difference between a free-electron gas and the tightly-bound electrons in an atom: If we select a specific electron $i$ located at a specific position $\mathbf{r}$ in a free-electron gas, the remaining electrons tend to stay away from the point $\mathbf{r}$ because of their electrostatic repulsion by electron $i$, and we have a decrease in potential energy because of the lower interaction of $i$ with the other electrons; at the same time, these other electrons have a large volume into which they can move and their repulsion by $i$ produces a negligible increase in electron density in other parts of the volume, and therefore negligible changes in the energies of the other electrons. In an atom, on the other hand, the electrons are confined to a very small volume; repulsion by a specific electron $i$ cannot be so effective as in a free-electron gas, and what energy gain does result from the reduced interaction between $i$ and the other electrons may be largely lost because these other electrons are forced closer together, with consequent increases in their kinetic and Coulomb energies.[35]

Clearly this effect is smallest at low electron densities, and the dashed curve in Fig. 1 will be asymptotically correct as $r_s \to \infty$. As $r_s$ decreases, the appropriate value of $e_c$ for electrons in an atom will depart increasingly further from the free-electron value. We estimate the magnitude of this effect with the aid of experimental results, which indicate that for neutral atoms with $Z \leqq 18$ the average correlation energy is about 0.08 rydbergs/electron (0.04 a.u./electron).[36] Thus we shall

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[29] M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106**, 364 (1957).

[30] W. J. Carr, Jr. and A. A. Maradudin, Phys. Rev. **133**, A371 (1964).

[31] L. Hedin, Phys. Rev. **139**, A796 (1965).

[32] D. Pines, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1955), Vol. I, p. 375.

[33] R. D. Cowan and J. G. Kirkwood, Phys. Rev. **111**, 1460 (1958).

[34] W. J. Carr, Jr., R. A. Coldwell-Horsfall, and A. E. Fein, Phys. Rev. **124**, 747 (1961).

[35] This same argument probably explains the fact that in the exchange approximation (12) or (14) the required value of $k_1$ is considerably smaller than the free-electron value $\frac{3}{2}$ (the exchange energy being simply a partial correlation energy among electrons of like spin, produced by effects of the Pauli exclusion principle)—as well as the fact that in the HFS and HFSL methods the value $k_x=1$ gives better wavefunctions than does $k_x=\frac{3}{2}$. At the same time, it may indicate that Slater's original value $k_x=\frac{3}{2}$ is better for application to free-electrons in solids; see J. C. Slater, Bull. Am. Phys. Soc. **11**, 511 (1966); Solid State and Molecular Theory Group MIT, 1965, Quarterly Progress Report No. 58 (unpublished).

[36] E. Clementi, J. Chem. Phys. **38**, 2248 (1963); **39**, 175 (1963); **42**, 2783 (1965).

replace (18) with the modified function

$$e_c(r_s) = -[4(r_s+9)^{1/2}+1.142r_s]^{-1} \tag{21}$$

shown as a solid curve in Fig. 1, which is a convenient (but arbitrary) interpolation formula between the low-density free-electron limit and a high-density limit $e_c \to -0.0833$ Ry; this function has been used in the expression (20) for the calculation of all correlation energies tabulated in this paper.

The expression for total correlation energy, together with the variational principle, can be used to derive a correlation pseudopotential[14,26] $V_c(r)$ analogous to the exchange pseudo-potential $V_{xs}(r)$ or $V_{xs}'(r)$. However, in this work we have preferred not to include $V_c$ in the potential $V^i$ used in the radial differential equation for the following reasons:

(1) The effects of including $V_c$ are small compared with those of $V_{xs}'$, but would at the same time make impossible direct comparison of HX with HF results, thereby making it difficult to distinguish effects of $V_c$ from effects due to (14) being a poor approximation to the HF exchange terms.

(2) Because of the energy-minimum principle, inclusion of $V_c$ would have almost negligible effects on the energy $E$ computed from (2) and on excitation or ionization energies $\Delta E$.

(3) Inclusion of $V_c$ would produce a more negative potential which would pull the electrons closer together, thereby increasing the computed values of the interaction parameters $F^k$ and $G^k$ (which are already nearly always greater than indicated by experiment[7]), even though physically the effect of correlation should be to keep electrons apart and thereby *reduce* their mutual interaction. (This paradox of course arises because we are working with spherically averaged wave functions, whereas the inherent nature of correlation effects is the introduction of local asymmetries.)

## IV. NUMERICAL RESULTS

All numerical results (other than HF) quoted in this paper were computed with a FORTRAN II program developed by the author for the IBM 7094. This program is based on the one written by Herman and Skillman[16] for HFS and HFSL calculations, with only minor modifications in basic numerical methods, but with the added possibility of the HX scheme (or sequential calculation according to any two or all three schemes), and the added calculation of all $F^k$, $G^k$, $\zeta_i$, $\langle r^n\rangle_i$, $(i|j)$, $E^i$, $E_r^i$, $E_c^i$, $E$, and $E_t \equiv E+E_r+E_c$.

Like the HF method, the HX scheme requires some sort of initial estimate of the wave functions $P_{nl}$, in order to provide the densities $\rho^i = P_i^2/4\pi r^2$ needed in (10), (11), (14) for calculation of the potential energy $V^i(r)$. These estimates are provided by first performing a HFSL calculation, which can be started in the Herman-Skillman manner using a universal input potential function [e.g., the function $U(x)$ tabulated by HS[16] for Ar, automatically scaled by the program to the appropriate value $-2Z$ at $r=0$]. After two or three iteration cycles under the HFSL scheme, the program automatically shifts to the HX scheme, and the iteration proceeds very stably to a final self-consistent result in a total of about 12–18 cycles. Total time requirements on the 7094, including calculation of the $F^k$, $G^k$, $\cdots$ on the final cycle, are about one minute for each 4 or 5 orbitals in neutral atoms [e.g., 1.3 min for $_{19}$K (6 orbitals) and 5 min for $_{92}$U (17 orbitals)], and one minute for each 6 or 7 orbitals in highly ionized atoms.

In Table I are compared some results for Ar I $3p^53d$ computed by various methods (the Hartree results having been obtained using the HX scheme with $k_1=0$). The HFS and HFSL results (except for the eigenvalues $\epsilon^i$) are significantly improved by using $k_x=1.0$ instead of 1.5. Additional improvement is afforded by the HX approximation, especially in the eigenvalues (from which automatically follows better values of $\langle r^6\rangle$).

The degree to which the HX results in Table I approximate HF values is typical of most configurations. Total energies are quite accurate (because of the variational principle), and will be discussed in greater detail below. Results for the Slater integrals are usually fairly good, except that values of the $G^k$ (with maximum $k$) involving an excited electron may be 25 to 50% larger than HF, especially when a considerable cancellation between positive and negative contributions to the integral is involved; this is not so serious as it may sound, since even HF values are frequently 50% greater than empirical values, for reasons already referred to.[7]

For the outer electrons, HX values of $\langle r^{-3}\rangle$ tend to be too large by as much as 50%. Partly as a result of this, values of the spin-orbit parameter computed from the one-electron formula

$$\zeta_i = \tfrac{1}{2}\alpha^2(i|r^{-1}dV^i/dr|i) \tag{22}$$

are generally 10 to 50% greater than values computed by Froese[20] using HF functions and the Blume-Watson theory;[37] the latter values are much more accurate for low $Z$, but the former usually agree better with experiment for $Z > \sim 30$.

HX wave functions of equal $l$ but different $n$ are not necessarily orthogonal. However, unlike Hartree wave functions in certain cases, the departures from orthogonality are not serious, overlap integrals being usually less than 0.01 for inner orbitals and seldom reaching values greater than 0.05 for outer incompletely-filled orbitals. No serious error has been observed to result from considering the HX functions as though they were exactly orthogonal.

Some additional comparisons between HX and HF

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[37] M. Blume and R. E. Watson, Proc. Roy. Soc. (London) **A270**, 127 (1962); **A271**, 565 (1963); M. Blume, A. J. Freeman, and R. E. Watson, Phys. Rev. **134**, A320 (1964).

TABLE III. HF and HX total binding energies (Ry)[a].

| Atom | HF[b] $E$ | HX $E$ | $E_r$ | $E_c$ | $E_t$ | exp[c] |
|---|---|---|---|---|---|---|
| He $1s^2$ | $-5.7234$ | $-5.7233$ | $-0.000$ | $-0.134$ | $-5.857$ | $-5.808$ |
| Li $2s$ | $-14.8655$ | $-14.871$ | $-0.002$ | $-0.157$ | $-15.030$ | $-14.957$ |
| Be $2s^2$ | $-29.1461$ | $-29.157$ | $-0.006$ | $-0.254$ | $-29.416$ | $-29.338$ |
| C $2p^2$ | $-75.3197$ | $-75.327$ | $-0.033$ | $-0.415$ | $-75.775$ | $-75.670$ |
| O $2p^4$ | $-149.539$ | $-149.536$ | $-0.112$ | $-0.582$ | $-150.230$ | $-150.156$ |
| $O^{6+}$ $1s^2$ | $-118.222$ | $-118.222$ | $-0.097$ | $-0.158$ | $-118.477$ | $-118.387$ |
| Ne $2p^6$ | $-257.095$ | $-257.078$ | $-0.291$ | $-0.749$ | $-258.118$ | $-258.1_2$ |
| Na $3s$ | $-323.720$ | $-323.705$ | $-0.441$ | $-0.782$ | $-324.928$ | $-324.8_9$ |
| Mg $3s^2$ | $-399.230$ | $-399.222$ | $-0.644$ | $-0.870$ | $-400.736$ | $-400.689$ |
| Al $3p$ | $-483.755$ | $-483.758$ | $-0.912$ | $-0.943$ | $-485.613$ | $-485.3_9$ |
| Ar $3p^6$ | $-1053.637$ | $-1053.678$ | $-3.732$ | $-1.353$ | $-1058.763$ | $-1058.62_0$ |
| Kr $4p^6$ | $-5504.114$ | $-5504.153$ | $-71.605$ | $-2.789$ | $-5578.547$ | ... |
| Xe $5p^6$ | $-14464.300$ | $-14464.375$ | $-399.613$ | $-4.216$ | $-14868.204$ | ... |
| Pb $6p^2$ | $-39047.992$ | $-39047.963$ | $-2306.665$ | $-6.490$ | $-41361.118$ | ... |

[a] Values are for the center of gravity of the ground configuration.

[b] C. Froese, Ref. 20; E. Clementi, J. Chem. Phys. **38**, 996, 1001 (1963); **41**, 295, 303 (1964); Pb from J. B. Mann, Jr., Ref. 22.

[c] C. E. Moore [*Atomic Energy Levels* (U. S. National Bureau Standards, Circular No. 467, U. S. Govt. Printing Office, Washington, D. C., 1949–1958, 3 vols.]; supplemented with theoretical values from J. D. Garcia and J. E. Mack [J. Opt. Soc. Am. **55**, 654 (1965)] and (for Ne and Ar) from Ref. 24.

values of total energy $E$ are included in Table III. However, this table is primarily intended to illustrate the accuracy which can be expected for correlation energies computed from (20) and (21), as indicated by a comparison with experiment of the total energy

$$E_t = E + E_r + E_c. \tag{23}$$

The errors in $E_c$ are rather large for small $N$, but on the whole results are probably about as good as can be expected from a statistical calculation.[38]

TABLE IV. HF and HX ionization energies (Ry).[a]

| Atom | HF[b] $\Delta E$ | HX $\Delta E$ | $\Delta E_r$ | $\Delta E_c$ | $\Delta E_t$ | exp[c] |
|---|---|---|---|---|---|---|
| O $2p^4$ | 1.071 | 1.067 | $-0.001$ | 0.069 | 1.135 | 1.164 |
| Al $3p$ | 0.404 | 0.412 | $-0.001$ | 0.054 | 0.465 | 0.439 |
| Si $3p^2$ | 0.524 | 0.526 | 0.000 | 0.057 | 0.583 | 0.572 |
| S $3p^4$ | 0.786 | 0.791 | $-0.001$ | 0.064 | 0.853 | 0.854 |
| Ar $3p^6$ | 1.086 | 1.088 | $-0.001$ | 0.067 | 1.154 | 1.163 |
| Ca $4s^2$ | 0.376 | 0.379 | 0.001 | 0.059 | 0.439 | 0.449 |
| Sc $3d4s^2$ | 1.287 | 0.406 | 0.003 | 0.055 | 0.465 | 0.488 |
| $Sc^+$ $3d4s$ |  | 0.889 | 0.006 | 0.043 | 0.937 | 0.942 |
| $Ss^{++}$ $3d$ | 1.756 | 1.745 | $-0.012$ | 0.069 | 1.802 | 1.819 |
| Cu $3d^{10}4s$ | 0.466 | 0.467 | 0.015 | 0.049 | 0.531 | 0.568 |
| $Cu^+$ $3d^{10}$ | 1.322 | 1.285 | $-0.012$ | 0.069 | 1.342 | 1.499 |
| Ge $4p^2$ | 0.508 | 0.516 | $-0.003$ | 0.057 | 0.570 | 0.554 |
| Ag $4d^{10}5s$ | 0.435 | 0.419 | 0.037 | 0.050 | 0.506 | 0.557 |
| Sn $5p^2$ | 0.483 | 0.465 | $-0.004$ | 0.056 | 0.517 | 0.516 |
| Xe $5p^6$ | 0.849 | 0.860 | $-0.002$ | 0.064 | 0.922 | 0.924 |
| Cs $6s$ | 0.254 | 0.255 | 0.008 | 0.026 | 0.289 | 0.286 |
| Au $5d^{10}6s$ | 0.385 | 0.426 | 0.109 | 0.052 | 0.587 | 0.678 |
| Pb $6p^2$ | 0.457 | 0.465 | $-0.010$ | 0.055 | 0.511 | 0.501 |

[a] Measured between centers-of-gravity of the ground configurations.

[b] E. Clementi, J. Chem. Phys. **38**, 996, 1001 (1963); **41**, 295, 303 (1964); J. M. Wilson, Ref. 21.

[c] C. E. Moore, *Atomfc Energy Levels* (U. S. National Bureau of Standards Circular No. 467, U. S. Govt. Printing Office, Washington, D. C., 1949–1958), 3 vols.

Similar comparisons for ionization energies rather than total energies are given in Table IV. Agreement of theory with experiment is quite good, except for cases involving full (or nearly full) $d$ shells near the outer edge of the atom. (The comparatively very large correlation energies existing in these cases have been discussed by Clementi.)[36]

For atoms with $Z$ greater than about 45, $|E|$ becomes greater than 10 000, and on an 8-significant-figure computer values of $\Delta E$ cannot be calculated to 0.001 Ry without being affected by roundoff error. However, in such cases the innermost orbitals ($q$, say, in number) can be considered identical in both atom and ion. We then define an energy $E'$ computed as in (2), except with the summation over $i$ extended only over electrons in orbitals $q+1$ to $q_{\max}$. If sufficient orbitals $q$ are thus deleted to keep $|E'|<5000$, say, then values of $\Delta E'$ will be arithmetically significant to three decimals, and

TABLE V. HX excitation energies (Ry) in Ar I.

| Config. | $\Delta E_r$ | $\Delta E_c$ | $\Delta E_t$ | exp[a] |
|---|---|---|---|---|
| Ar I $3p^6$ | 0 | 0 | 0 | 0 |
| $3p^54s$ | $-0.002$ | 0.043 | 0.845 | 0.856 |
| $3p^54p$ | $-0.001$ | 0.056 | 0.956[b] | 0.968 |
| $3p^53d$ | $-0.001$ | 0.059 | 1.030[b] | 1.035 |
| $3p^54f$ | $-0.001$ | 0.067 | 1.093 | 1.100 |
| $3p^55g$ | $-0.001$ | 0.067 | 1.116 | 1.123 |
| Ar II $3p^5$ | $-0.001$ | 0.067 | 1.156 | 1.163 |

[a] C. E. Moore [*Atomic Energy Levels* (U. S. National Bureau of Standards, Circular No. 467, U. S. Govt. Printing Office, Washington, D. C. 1949–1958), 3 vols]; and C. J. Humphreys, E. Paul, Jr., R. D. Cowan, and K. L. Andrew [J. Opt. Soc. Am., **57**, 855 (1967)]. Energy differences are between configuration centers of gravity.

[b] The HF values, using the above values of $\Delta E_r$ and $\Delta E_c$, are 0.956 Ry and 1.027 Ry. (J. B. Mann, Jr., Ref. 22).

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[38] The error for $N=2$ is due to the fact that Eq. (20) really counts the correlation energy twice. Indeed, nearly all the results in Table III can be improved by deleting the correlation energy of one of the $1s$ electrons ($\cong -0.07$ Ry).

Table VI. Energies (in Ry) of excited configurations of the noble gases, measured relative to the ions.

| Config. | $E^i$ [a] | $\Delta E_c$ | $\Delta E_t$ Calc | $\Delta E_t$ Exp[b] |
|---|---|---|---|---|
| Ne $2p^6 4f$ | −0.06250 | −0.00004 | −0.06254 | −0.06255 |
| Ar $3p^6 4f$ | −0.06251 | −0.00018 | −0.06269 | −0.06277 |
| Kr $4p^6 4f$ | −0.06252 | −0.00032 | −0.06284 | −0.06292 |
| Xe $5p^6 4f$ | −0.06256 | −0.00056 | −0.06312 | −0.06325[c] |
| Ne $2p^5 5g$ | −0.04000 | −0.00000 | −0.04000 | −0.04001 |
| Ar $3p^5 5g$ | −0.04000 | −0.00000 | −0.04000 | −0.04003 |
| Kr $4p^5 5g$ | −0.04000 | −0.00001 | −0.04001 | −0.04005[c] |
| Xe $5p^5 5g$ | −0.04001 | −0.00002 | −0.04003 | −0.04009[c] |

[a] The hydrogenic values are $E^{4f}=-0.0625$ Ry and $E^{5g}=0.04$ Ry. The HF values (J. M. Wilson, Ref. 21) for the $4f$ configurations are identical with the HX values to four significant figures.

[b] C. E. Moore, *Atomic Energy Levels* (U. S. National Bureau of Standards, Circular No. 467, U. S. Govt. Printing Office, Washington, D. C., 1949–1958), 3. vols; C. J. Humphreys, E. Paul, Jr., R. D. Cowan, and K. L. Andrew, J. Opt. Soc. Am., **57**, 855 (1967).

[c] Measured between the centers-of-gravity of the levels with $j_1=\frac{3}{2}$, as the $j_1=\frac{1}{2}$ levels have not been observed experimentally.

will still include the effects of relaxation of the outer orbitals upon ionization. The values of $\Delta E$ given in Table IV for heavy atoms have all been computed in this way.

The most critical test of the accuracy of energy calculations lies in values of excitation energies. Some computed results for argon are given in Table V; the good agreement between calculated and experimental energies indicates that the variation of $\Delta E_c$ with configuration is given fairly accurately by the statistical calculation.

In the case of excited states of heavy atoms involving very nearly hydrogenic orbitals, such as the configurations $p^6 4f$ and $p^5 5g$ in Kr and Xe, even the previously mentioned values of $\Delta E'$ (in place of $\Delta E$) cannot be depended on for high-accuracy values of ionization energy. However, the fact that the $4f$ and $5g$ eigenvalues are nearly hydrogenic means that these electrons penetrate the core only slightly so that their removal produces little change in the core wave functions. The conditions of Koopmans's theorem are then well satisfied, and the one-electron binding energy becomes a valid measure of $E_{\text{av}}$, measured downward from the ground-configuration (center-of-gravity) energy of the ion. Energies determined in this way for the noble gases are shown in Table VI. Relativistic corrections are negligible, and correlation corrections $\Delta E_c$ are computed relative to the ion. Elimination of the self-correlation energy through use of (20) [rather than (19)] is essential in cases such as these, where the excited electron barely penetrates the core. The fairly good agreement with experiment shows that at large $r_s$ the free-electron correlation energy (the dashed curve in Fig. 1) is applicable without modification to electrons in atoms, as assumed in Eq. (21).

## V. SUMMARY

The HX scheme, equivalent to Hartree's original SCF method plus the additional potential term (14) as a statistical approximation to the exact quantum-mechanical exchange terms, does not of course provide radial wave functions identical with the HF ones. However, it does seem fairly satisfactorily to have provided a calculational method which: (a) is computationally much simpler than HF; (b) is almost completely free of iteration-instability problems; (c) requires no accurate nor elaborate parameters to start the calculation (the only requirements being a universal starting potential function plus specification of the configuration of interest—though moderately accurate estimates of the orbital eigenvalues will save some computer time); (d) is free of the HFS method's inadequate binding of excited orbitals, and of the HFSL method's incorrect ionization energies of excited configurations; (e) gives eigenvalues approximately equal to the quantum-mechanical one-electron binding energies, and total energies which closely satisfy the virial theorem; and (f) gives values of energy, interaction parameters $(F^k, G^k, \zeta_i)$ and $\langle r^n \rangle$ which agree with experiment about as well as do HF values. For problems in which HF accuracy is required, the HX method may still be useful for providing starting information for HF calculations, and it has in fact been used for this purpose with considerable success. It seems clear that a practical unified three-stage program could be written which would begin a calculation with two or three iteration cycles under the HFSL scheme, continue with a few HX cycles, and conclude with iteration to a self-consistent HF result.

Calculation of correlation energies based on statistical free-electron results requires introduction of certain modifications for application to bound electrons in atoms. The results are only moderately accurate, but are worth computing for many-electron atoms where more accurate methods are computationally impractical.

## ACKNOWLEDGMENTS

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