PHYSICAL REVIEW
LETTERS

VOLUME 22 21 APRIL 1969 NUMBER 16

IMPROVED STATISTICAL EXCHANGE APPROXIMATION FOR INHOMOGENEOUS MANY-ELECTRON SYSTEMS*

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(Received 17 March 1969)

We have developed an improved exchange approximation for use in self-consistent atomic structure calculations and related problems. By adding an inhomogeneity correction to the Kohn-Sham-Gaspar exchange potential, we are able to obtain total energies for atoms that are consistently closer to the Hartree-Fock values than are those given by other recently proposed exchange potentials.

Slater's simplified treatment[1] of the exchange terms in the Hartree-Fock equations for many-electron systems has proved extremely useful in a wide variety of applications, most notably atomic-structure[2,3] and energy-band calculations.[4] During the past few years, several variations and refinements of Slater's $\rho^{1/3}$ exchange approximation have been proposed and critically examined.[5-9] In this paper we report an improved exchange approximation which leads to lower total energies than earlier exchange approximations, including some which are momentum dependent.[8,9] Our approach is quite simple and is well adapted to atomic, molecular, and solid-state calculations.

The novel feature of our approach is the introduction of an exchange-inhomogeneity correction involving second-order terms in $|\nabla\rho|$ reminiscent of the Weizsäcker inhomogeneity correction in the statistical theory of atoms.[10-12] Apart from the substantial improvement in the total energy, the introduction of the exchange-inhomogeneity correction simplifies the treatment of the dominant $\rho^{1/3}$ exchange term: Instead of having to assign slightly different coefficients to this last term for different atomic systems, it is possible to use the same (Kohn-Sham-Gaspar)[5] coefficient for a large class of such systems.

In order to arrive at the proper form for the exchange-inhomogeneity correction, we will make use of a dimensional argument followed by a variational calculation. Beginning with the standard expression for the total energy of a many-electron system in the statistical field approximation,[12] we insert a new term (representing the exchange-inhomogeneity correction) which depends only on ρ and $|\nabla\rho|^2$ and has the same dimensions as the usual exchange term. (We could easily extend our argument to include, say, fourth-order terms in $|\nabla\rho|$, but we will confine our attention to second-order terms in $|\nabla\rho|$, since these undoubtedly account for the principal inhomogeneity effects.)

Expressing energies in Rydbergs and distances in Bohrs, we have for the total energy in the statistical field approximation

$$E=\int\left[C_{\mathrm{K}}\rho^{5/3}+V\rho+C_{\mathrm{XH}}\rho^{4/3}+C_{\mathrm{XI}}\frac{|\nabla\rho|^2}{\rho^{4/3}}+C_{\mathrm{W}}\frac{|\nabla\rho|^2}{\rho}\right]d\tau, \quad (1)$$

where the first three terms represent the kinetic, potential, and standard exchange energies, while the fourth and fifth terms represent the exchange and Weizsäcker inhomogeneity corrections, respectively. (Although we do not intend to make any direct use of the Weizsäcker term in the sequel, we are carrying this along so that the reader can see the parallel with the new exchange-inhomogeneity term. It should be borne in mind, however, that the Weizsäcker term has the same dimensions as the kinetic-energy term.) For the moment, we will assume that V is independent of ρ, and that the various coefficients appearing in Eq. (1) are fixed quantities.

Minimizing the above expression for E by the usual techniques of the calculus of variations,[12] we obtain the following differential equation (Euler characteristic equation) for ρ:

$$(5/3)C_K\rho^{2/3} + V + \tfrac{4}{3}C_{XH}\rho^{1/3} + C_{XI}\rho^{1/3}G_{XI}(\rho) + C_W\rho^{2/3}G_W(\rho) = E', \qquad (2)$$

where E' is a Lagrangian multiplier related to the total number of electrons, and the dimensionless G functions are defined as follows:

$$G_{XI}(\rho) = \frac{1}{\rho^{2/3}}\left[\frac{4}{3}\left(\frac{\nabla\rho}{\rho}\right)^2 - \frac{2\nabla^2\rho}{\rho}\right];$$

$$G_W(\rho) = \frac{1}{\rho^{2/3}}\left[\left(\frac{\nabla\rho}{\rho}\right)^2 - \frac{2\nabla^2\rho}{\rho}\right]. \qquad (3)$$

Since we know that the solution of Eq. (2) for ρ minimizes the total energy, the various terms appearing in this equation must have special properties. We already know from earlier work[1-9] that $\rho^{1/3}$ provides a remarkably good first approximation for exchange. Hence, we regard $\rho^{1/3}G_{XI}(\rho)$ as the natural form for the exchange-inhomogeneity correction. This view is bolstered by the following consideration: If we had used the alternative second-order term $\nabla^2\rho\rho^{-1/3}$ in Eq. (1) instead of $|\nabla\rho|^2\rho^{-4/3}$, the variational calculation would have led to the same functional form for $G_{XI}(\rho)$.[13] Accordingly, we propose the following improved exchange approximation:

$$V_{\text{exch}}(\vec{r}) = V_{\text{exch}}[\rho(\vec{r})] = [\alpha + \beta G_{XI}(\rho)]V_{XS}(\rho), \qquad (4)$$

where $V_{XS}(\rho)$ denotes the original Slater exchange approximation[1]

$$V_{XS}(\rho) = -6\left[\frac{3}{8\pi}\rho\right]^{1/3}, \qquad (5)$$

and α and β are coefficients which replace the coefficients C_{XH} and C_{XI} appearing earlier.

In the case of a homogeneous electron gas, it is well known[5] that a variational calculation (minimizing the total energy) leads to a value of $\alpha = \frac{2}{3}$. Of course, for such a gas $G_{XI}(\rho) = 0$. As has been recognized for some time,[5,6] and as the representative results shown in Table I clearly indicate, in applications to inhomogeneous systems such as atoms the Kohn-Sham-Gaspar exchange approximation $V_{XKSG}(\rho) = \frac{2}{3}V_{XS}(\rho)$ leads to total energies that are considerably closer to the Hartree-Fock values than are those given by the Slater approximation.[14] It is possible to bring the total energy still closer to the Hartree-Fock value by replacing the factor of $\frac{2}{3}$ in front of $V_{XS}(\rho)$ by an adjustable parameter α and finding a value for α which minimizes the total energy. Although this so-called Xα scheme[9] is quite simple to carry out for atomic and molecular systems, for which the total energy can be calculated with a high degree of accuracy, it is somewhat inelegant in the sense that the optimum value of α varies from atom to atom (cf. Table I). By the optimum value we mean the value that minimizes the total energy.

At first glance, it might appear that the present exchange approximation, as embodied in Eq. (4), is merely a two-parameter generalization of the one-parameter Xα scheme. According to this point of view, the values of α and β, in what we will henceforth call the X$\alpha\beta$ scheme, are to be chosen so that the total energy of the system is minimized.

After carrying out a number of atomic calculations in this spirit, we were delighted to discover that, within the accuracy of our calculations, the optimum value of α turned out to be $\frac{2}{3}$, as in the Kohn-Sham-Gaspar approximation,[5] while the optimum value of β differed slightly from atom to atom. Thus, by introducing the inhomogeneity term, it is possible to assign the same value of α to all atoms ($\alpha = \frac{2}{3}$), thereby restoring the elegance of the dominant exchange term. Of course, in the process, the inelegance is shifted to the inhomogeneity term, but this is, after all, a relatively small term.

If indeed α is set equal to $\frac{2}{3}$, then the X$\alpha\beta$ scheme is reduced to a one-parameter scheme, involving now only the adjustable parameter β. Although we will continue to call our scheme the X$\alpha\beta$ scheme, to distinguish it from the closely related but less general Xα scheme, it will be

Table I. Comparison of total energies and optimum parameters for four representative atomic systems as given by various exchange approximations.[a] Total energies are expressed in Rydbergs and have been multiplied by −1.

Exchange approximation	Ar	Cu^+	Kr	Xe
V_{XS} (Slater $\rho^{1/3}$; $\alpha=1$)	1053.36	3276.94	5503.48	14 463.33
V_{XKSG} (Kohn-Sham-Gaspar $\rho^{1/3}$; $\alpha=\frac{2}{3}$)	1053.59	3277.34	5504.02	14 464.17
V_{XL} (Liberman, momentum dependent)	...	3277.33[b]	...	...
V_{XLSW} (modified Liberman, momentum dependent)	...	3277.36[b]	...	...
$V_{X\alpha}$ (optimized $\rho^{1/3}$)	1053.60	3277.37	5504.03	14 464.17
$V_{X\alpha\beta}$ (present work)	1053.62	3277.39	5504.08	14 464.25
V_{XHF} (Hartree-Fock)	1053.635[c]	3277.46[c]	5504.11[c]	14 464.28[c]
$V_{X\alpha}$: optimum value for α	0.713	0.738	0.700	0.688
	±0.005	±0.008	±0.005	±0.005
$V_{X\alpha\beta}$: optimum value for β ($\alpha=\frac{2}{3}$)	0.004	0.005	0.005	0.005
	±0.001	±0.001	±0.001	±0.001

[a] The XS approximation is described in Refs. 1 and 2; XKSG in Ref. 5; XL in Ref. 8; XLSW and Xα in Ref. 9. The Latter tail correction (cf. Ref. 2) was not used in arriving at our own entries for XS, XKSG, Xα, and X$\alpha\beta$ above.

[b] Ref. 9. In this reference, the following values are quoted for Cu^+: XS, 3276.96; XKSG, 3277.23; and Xα, 3277.30, with $\alpha=0.77$. These values differ from ours because the Latter tail correction was used in this reference. We cannot tell from Ref. 9 whether the omission of the Latter correction would improve the total energy (as for XKSG and Xα), or degrade it (as for XS).

[c] J. B. Mann, Los Alamos Report No. LA 3690, July 1967 (unpublished).

understood in what follows that we are setting α equal to $\frac{2}{3}$ and treating only β as an adjustable parameter. For an inhomogeneous electron system specified in terms of ρ, $\nabla\rho$, and $\nabla^2\rho$, it would be most helpful to have a first-principles value for β, just as we now have a first-principles value for α for a homogeneous electron gas.[5] But in the absence of a fundamental value for β, we are compelled to determine β by minimizing the total energy with respect to β.

Although our exchange approximation [cf. Eq. (4)] is well behaved for most values of r, as can be seen from Fig. 1, special care must be taken at extremely small and extremely large values of r (in atomic systems). Because of the presence of the $\nabla^2\rho\rho^{-4/3}$ term in $G_{XI}(\rho)$, $V_{exch}(\rho)$ varies as $1/r$ as $r\to 0$. (The divergent behavior of terms involving $\nabla^2\rho$ near atomic nuclei has already been noted by Ma and Brueckner[15] in a related discussion of the correlation energy of an inhomogeneous electron gas.) Although it is possible, and perhaps even desirable, to modify $G_{XI}(\rho)$ so as to eliminate the $1/r$ behavior at small values of r, we have not done so to date, largely because this behavior appears to have only a minor effect on most of our results. The only results noticeably affected are the values of s-like wave functions at the nucleus.

At large values of r, the function V_{exch} blows up, just as exact Hartree-Fock exchange potentials do.[9] Although energy integrals involving V_{exch} are convergent, the blowup at large values of r is a computational nuisance from the standpoint of our atomic-structure computer codes.[2] For convenience, we have multiplied $G_{XI}(\rho)$ by a convergence factor which eliminates the blowup; the detailed form of this factor affects the final results to an insignificant degree. The convergence factor is incorporated in Eq. (4) by replacing $G_{XI}(\rho)$ by $G(\rho)$, where

$$G(\rho)=G_{XI}(\rho)\exp\left[-\frac{3}{2}\frac{\beta_0}{\rho^{2/3}}\left(\frac{\nabla\rho}{\rho}\right)^2\right], \tag{6}$$

with β_0 approximately equal to β. In applications to crystals, it would not be necessary to use this convergence factor since ρ does not usually become sufficiently small anywhere in the unit cell to induce the blowup.

The optimized exchange potentials for atomic Kr, as given by the Xα and X$\alpha\beta$ schemes, are compared in Fig. 1. It can be seen that the inclusion of the inhomogeneity term leads to more

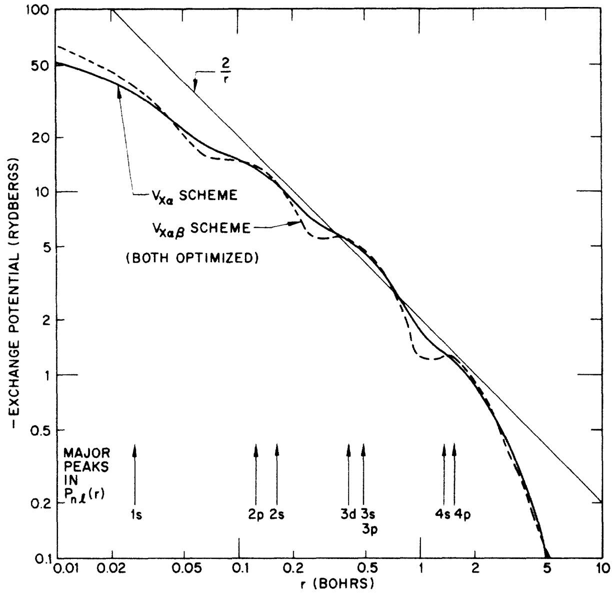

FIG. 1. Comparison of the exchange potentials for atomic krypton, according to optimized $\rho^{1/3}$ ($V_{X\alpha}$) and present ($V_{X\alpha\beta}$) schemes. The function $2/r$ is shown for reference. The positions of the major peaks in the atomic orbitals $P_{nl}(r)$ are also indicated.

pronounced variations in the magnitude of the exchange potential. The modulation produced by the inhomogeneity term is of the order of 10%.

The relative merits of various exchange approximations can be judged in a number of ways, including (a) how closely the energy eigenvalue spectrum compares with the experimental excitation spectrum,[2-9] (b) how closely the calculated values of total energy, one-electron binding energies, one-electron energy eigenvalues, electronic charge distributions and their moments, and various matrix elements (such as I, F, and G integrals) compare with their Hartree-Fock counterparts,[5-9] and (c) how convenient it is to carry out the calculations for realistic physical systems.

An important virtue of our exchange approximation is that it leads to total energies that are consistently closer to their Hartree-Fock counterparts than are those given by other exchange approximations.[1,5-9] This statement is illustrated in Table I, where we compare the total energies for four representative atomic systems obtained on the basis of the most widely discussed exchange approximations. Further comparisons between our results and those obtained by other methods will be reported elsewhere.[16]

The lowering of the total energy produced by the presence of the inhomogeneity term is not accidental: It should be recalled that the form of the inhomogeneity term was established from a variational calculation whose aim was the minimization of the total energy [cf. Eqs. (1) and (2)]. The inclusion of the inhomogeneity term changes the magnitude and shape of the exchange potential, as can be seen from Fig. 1; this in turn changes the detailed shapes of the various atomic orbitals. As a consequence, there is a delicate readjustment of kinetic-, potential-, and exchange-energy contributions to the total energy, leading to a lowering of the total energy.

Although the virial theorem is very nearly satisfied when α is assigned its optimum value in the $X\alpha$ scheme, or when β is assigned its optimum value in the $X\alpha\beta$ scheme (with $\alpha = \frac{2}{3}$), the ratio of potential and kinetic energies is not exactly −2. (The deviation from −2 is usually quite small.) If one attempts to rescale[17] the kinetic and potential energy contributions so that the virial theorem is satisfied exactly, the total energy can be lowered still further, but only by a negligible amount.

In summary, we have developed an improved exchange approximation which leads to lower total energies than other recently proposed exchange approximations. Apart from this desirable feature, we are able to assign the same coefficient to the dominant $\rho^{1/3}$ exchange term for a wide variety of atomic systems, namely, the Kohn-Sham-Gaspar coefficient of $\frac{2}{3}$. In atomic and molecular structure calculations, where it is possible to calculate the total energy, the coefficient of the inhomogeneity correction term can be determined by carrying out a series of calculations and finding what coefficient minimizes the total energy. In energy-band calculations, where the principal interest focuses on the energy eigenvalue spectrum, the coefficient of the inhomogeneity correction can be treated as an empirical parameter.[4] In view of its inherent simplicity, and its many attractive features, it is expected that the present exchange approximation ($X\alpha\beta$ scheme) will prove useful in a variety of applications.

The authors wish to acknowledge interesting discussions with Mr. Thomas H. DiStefano of Stanford University and Dr. Roy A. Berg of Lockheed Research Laboratory.

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*Research supported in part by the Lockheed Independent Research Fund and in part by the Aerospace Research Laboratories, Office of Aerospace Research, under Contract No. F33615-67-C-1793.

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ACCURATE ROTATIONAL CONSTANTS OF $C^{12}O_2^{16}$ FROM MEASUREMENT OF cw BEATS IN BULK GaAs BETWEEN CO_2 VIBRATIONAL-ROTATIONAL LASER LINES

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(Received 4 March 1969)

A room-temperature bulk GaAs mixer is used to mix frequencies of pairs of cw vibrational-rotational CO_2 laser lines, each stabilized to line center. The beat frequencies, in the millimeter-wave region of 50-80 GHz, are measured for 37 pairs of transitions to better than 1 MHz. The deduced rotational constants for the relevant vibrational levels (00^01, 10^00, 02^00) are 25 to 200 times more accurate than the best previous results (from conventional spectroscopy).

In this Letter we report the cw beating of pairs of CO_2 vibrational-rotational laser lines near 10 μ, in room-temperature bulk GaAs. The beat frequencies (which lie in the 50- to 60- and 70- to 80-GHz millimeter-wave region) were measured for 37 pairs of lines to an accuracy, in most cases, of much better than 1 MHz. From these measurements we have calculated the rotational constants of the 10^00, 02^00, and 00^01 vibrational levels of $C^{12}O_2^{16}$. These constants have 25 to 200 times better accuracy than the best spectroscopic determinations to date. They also have the advantage of being direct frequency measurements rather than the wavelength measurements of conventional spectroscopy and refer to the molecule unperturbed by pressure effects.

Beats between CO_2 laser lines have recently been reported in metal-metal point-contact diodes[1] and in bulk GaAs.[2] The present work is a continuation of that described in Ref. 2 and uses the same bulk GaAs infrared mixer. By using two cw feedback stabilized lasers instead of a single Q-switched laser oscillating simultaneously on two or more lines, we are now able to measure a much larger number of beat frequencies with far greater accuracy than in the previous experiments.

The two lasers used a flowing gas mixture of CO_2, N_2, and He with approximate partial pressures of 1, 2, and 10 Torr, respectively. Each had a diffraction grating as one end mirror and could be tuned to oscillate on at least 43 separate transitions in the P and R branches of the 00^01-10^00 (10.4-μ) and 00^00-02^00 (9.4-μ) bands of CO_2. A piezoceramic mount for the curved dielectric mirror on the other end of the 2-m cavity enabled us to use feedback to stabilize each laser to the center of a chosen line, with a short-term stability of better than 10^5 Hz. The feedback control was obtained by vibrating the curved mirrors of both lasers synchronously at 84 Hz, then demodulating the resulting small amplitude modulation on the laser output with a phase-sensitive detection system, and finally feeding the ampli-