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6. AUTHOR(S) Joseph B. Krieger					
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13. ABSTRACT (Maximum 200 words) In this final year of the grant period, we have concentrated our efforts in three areas: (1) The determination of the exact exchange mixing parameter by requiring that the ionization energy theorem for atoms with $Z \leq 20$ be satisfied as closely as possible, (2) the completion of the application of Kohn-Sham Theory for Orbital Dependent (Self-Interaction-Corrected) Exchange-Correlation Energy Functionals to Diatomic Molecules and (3) The development of a new accurate, zero parameter, correlation energy functional obtained from the homogeneous electron gas with an energy gap and its application to the calculation of the ionization potentials and electron affinities of atoms. This approach is the first one that takes explicit account of the non zero energy of excitation for bound electrons. The functional includes the important self-interaction effects employing a method that is invariant under a unitary transformation. In both (1) and (2) the KLI approximation is employed to provide an accurate solution to the integral equation for the Optimized Effective Potential.					
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A. Statement of the Problem Studied.

Density functional theory provides in principle a method for the calculation of the exact ground state properties of any quantum mechanical system, e.g. atoms, molecules or solids. In order to apply this theory, the exchange-correlation energy which is in principle a functional only of the spin densities of the system, must be approximated. The standard local spin density (LSD) approximation and its related generalized gradient approximations (GGA) have had some significant success in providing quantitative and semi-quantitative understanding of molecular and solid state properties. However, these approximations do not provide a reliable framework for a truly quantitative method for the following reasons.

Both the LSD approximation and the GGA's do not yield the correct long range behavior of the Kohn-Sham exchange-correlation potential. This leads to the energy eigenvalue of the highest lying occupied orbital being in error by approximately 40% so the ionization theorem is not even approximately satisfied. Furthermore, these approximations do not provide for a discontinuity in the Kohn-Sham potential when a new subshell begins to be occupied, which leads to non-integer numbers of electrons on each atom when heteropolar molecules are pulled apart. And finally, although the application of the GGA significantly reduces the error in the LSD approximation, it still does not yield results for the ionization potential, electron affinity or the molecular dissociation energy that satisfy the quantum chemistry accuracy criteria. In fact neither the LSD or GGA yields stable negative ions.

It has been the purpose of this research project to develop a systematic approach that overcomes these difficulties and provides a method that can be reliably employed for accurate calculations of ground state properties of quantum systems, particularly for atoms and molecules for which the LSD approximation is least satisfactory.

B. SUMMARY OF THE MOST IMPORTANT RESULTS

During the course of this grant, we have made significant progress in providing a general solution to the problem studied as indicated below. (References indicated below refer to those given in the list of publications since inception of the grant).

First of all, we (Krieger, Li and Iafrate) have developed a method (generally referred to in the literature as the KLI approximation) that provides the Kohn-Sham spin polarized potentials, $V_{xc\lambda}$, for any orbital dependent exchange-correlation energy functional (1). We have shown analytically that the approximate $V_{xc\lambda}$ satisfies some important analytic properties exhibited by the exact result i.e. $V_{xc\lambda} \rightarrow V_{xc\lambda}(\text{LSD})$ in the homogeneous electron gas limit; $V_{xc\lambda}$ has the correct ($\rightarrow -1/r$) behavior in the large r limit; $V_{xc\lambda}$ changes discontinuously when a new spin subshell begins to be filled; the value of $V_{xc\lambda}$ averaged over the highest energy single particle state exactly equals the average value of the corresponding single particle exchange-correlation potential in a multi-potential (e.g. Hartree-Fock) theory. In addition, Janak's theorem is satisfied to within $\approx 0.2\%$.

Furthermore, we have also demonstrated numerically that the KLI approximation yields almost the exact exchange potential for atoms in the exchange-only case.

As a consequence of the correct analytic properties and the numerical accuracy of the resulting potential, we have shown that in the exchange-only case, the KLI approximation yields total energies for atoms within a few ppm from the exact result, the energy eigenvalue of the highest occupied orbital of both spin projections is within 0.2% of the exact result and the separate spin densities are nearly identical to the exact ones. Thus the expectation values of r^{-2} (which is proportional to the diamagnetic susceptibility) to the density at the atomic nucleus, are

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given with high accuracy.

Moreover, unlike the LSD or GGA's, self-consistent calculations employing the KLI method yield bound states for negative ions with total energies, highest occupied energy eigenvalues and spin densities as accurate as those obtained for neutral atoms. In addition, we have shown that as a consequence of the integer discontinuity in the potential, the principle of integer preference is satisfied when a heteropolar molecule is pulled apart e.g. when the interatomic distance for the NaCl molecule is large compared to the atomic radii, the energy minimizes for neutral Na and neutral Cl instead of transferring 0.4 electrons from Na to Cl as given by the LSD approximation.

The KLI method discussed above employs the full Hartree-Fock expression for the exchange-energy functional. For applications to systems containing many atoms this can present an involved numerical calculation. In order to ameliorate this problem, we have shown (12) that the method may be significantly simplified while maintaining the same level of accuracy for the calculation of those properties that depend on the valence electron orbitals. This method employs the LSD with self-interaction-correction (SIC) for the "core" electrons i.e. the electron states below the last two partially filled spin sub-shells of each atom. The remaining core-valence and valence-valence interactions are still treated exactly. Using this approximation we find that, as expected, the total energy is now only as accurate as that given by the LSDSIC energy functional because the "core" electrons make the predominant contribution to this quantity.

However, the ionization potential, the electron affinity, the expectation value of r^{-2} and the highest orbital energy eigenvalue are all given with an accuracy that is equivalent to the exact

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treatment of the exchange interaction in the KLI approximation.

The above analysis was restricted to the exchange-only case because the correlation energy functional, E_c is not exactly known. However, in order to obtain physically meaningful results for the ionization potential, I , and electron affinity, A , of atoms it is necessary to make some approximation for E_c . We have employed the LSDSIC approximation (2, 3) and the KLI method to obtain I and A for atoms with $Z \leq 20$. These results are a distinct improvement over those obtained by employing LSD alone, although they do not satisfy the quantum chemistry accuracy criterion (i.e. $1 \text{ kcal/mole} \approx 1.6 \text{ milli hartree/atom}$).

This fact has prompted further research into the nature of the exact Kohn-Sham potential for atoms (4, 8) and a comparative study of Kohn-Sham potentials in spin density and orbital i.e. self-interaction-corrected, functional theory (6, 9). Our results demonstrate that the addition of the SIC not only leads to a significant improvement of the total energy calculations, but also provides a substantial improvement in the Kohn-Sham potential, especially in the region of configuration space in which the valence electrons move. These are the first Kohn-Sham calculations which demonstrate an approximate satisfaction of the ionization energy theorem to within a few percent whereas the LSD and GGA result in $\approx 40\%$ errors.

These results have encouraged us to apply the KLI method to the calculation of molecular properties with the exchange-correlation energy functional given by the LSDSIC approximation.

The results of these calculations (7, 10, 11, 16) demonstrate that the predicted values of the total energy and the dissociation energy of diatomic molecules can be significantly improved by including the SIC. In addition, the calculated highest occupied orbital energy eigenvalue is

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close to the negative of the ionization potential in approximate agreement with the ionization energy theorem, which is known to be valid if the as yet unknown exact exchange-correlation energy functional were employed. However, the predicted interatomic bond lengths are not as accurate as given by the LSD approximation alone, and the predicted vibrational frequencies are far less accurate than provided by the LSD approximation.

These results have led us (13) to improve on the LSDSIC exchange-correlation energy functional by attempting to include some exact exchange mixing in the correlation energy functional as first proposed by Becke. Subsequently (14, 15), we have demonstrated that it is possible to derive the mixing parameter by purely theoretical considerations. This was accomplished by requiring that the ionization energy theorem be satisfied as closely as possible, i.e. that the calculated energy eigenvalue of the highest occupied state obtained by the KLI method be equal to the difference in energy of the N and $N-1$ electron system for atoms with $Z \leq 20$.

The resulting mixing parameter was thus found to be very nearly identical to that obtained by numerical fitting by others to the experimental results for the ionization potential. In addition, employing the same mixing parameter, we demonstrated that our results for the negative ions also closely satisfied the theorem and were in good agreement with experimental results without any further adjustments despite the fact that the LSD predicts all these negative ions are unstable. However, the difficulty encountered in the calculation of the properties of homopolar molecules (11, 16) due to the lack of invariance of the conventional Perdew-Zunger SIC under a unitary transformation of the occupied orbitals cannot be ameliorated in this way.

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These investigations have led us to a more intensive investigation of the correlation energy functional. Whereas the exact exchange energy functional is a known functional of the occupied orbitals of the system i.e. the Hartree-Fock expression, the exact correlation energy can only be expressed by perturbation theory as an infinite series in the coupling constant. In fact, for the homogeneous electron gas, each term in this series diverges, although in the high density limit the series can be summed using the techniques of many body perturbation theory as first done by Gellmann and Bruckner. Numerical results for physical densities have been obtained by Ceperley and Alder which form the basis of the LSD approximation. It is, however, well known for the past 30 years that the LSD for E_c for atoms overestimates the true E_c by more than a factor of two for light atoms with an error this is still $\sim 80\%$ for Argon.

As Walter Kohn, the founder and principal developer of this theory has said (NATO ASI in Density Functional Theory, 1993) the reason for this is that, unlike the case of the homogeneous electron gas, atoms have energy gaps so that the energy denominators in perturbation theory are non-zero. This gives rise to the convergence of the perturbation theory expansion for E_c after a couple of orders for atoms. It thus appears that if a proper density functional theory for the correlation energy is to be constructed, it must inherently include the existence of finite energies of excitation as found in atoms and molecules. In addition, it must include an SIC which is invariant under unitary transformation.

We have made significant progress in developing such a theory (17, 18) in collaboration with Dr. Andreas Savin, CNRS, Paris. We have demonstrated that it is possible to develop an accurate, zero parameter correlation energy functional from calculations employing the

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homogeneous electron gas with an energy gap. Once the resulting correlation energy functional is made self-interaction-free by a modification of an orbital dependent method initially suggested by A. Becke (private communication) which is also parameter free, we find that the correlation energy for atoms and their positive ions with $Z \leq 20$ is in error by only $\approx 5\%$ of the corresponding LSD error.

We are currently attempting to incorporate the known small gradient corrections applicable to the inhomogeneous electron gas into this formalism. Once this aspect is completed, this functional, together with the exact exchange energy functional, will form the basis of self-consistent calculations employing the KLI approximation to obtain the Kohn-Sham potential and the corresponding orbitals to calculate the properties of atoms and molecules. On the basis of our preliminary results, we are optimistic that this functional will provide the most accurate first principles calculation of the correlation energy functional yet proposed.

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C. List of all publications since inception of this grant.

- 1) Recent Developments in Kohn-Sham Theory for Orbital Dependent Exchange-Correlation Energy Functionals, J.B. Krieger, Y. Li and G.J. Iafrate (in "Density Functional Theory" eds. E.K.U. Gross and R.M. Dreizler, Plenum Press, New York, 1995).
- 2) Kohn-Sham Theory for Orbital Dependent Exchange-Correlation Energy Functionals: Application to the Calculation of Ionization Potentials and Electron Affinities, J.B. Krieger, Jiqiang Chen, Yan Li and G.J. Iafrate, Invited Talk presented at Sanibel Quantum Chemistry Symposium, February 1995.
- 3) Kohn-Sham Theory for Orbital Dependent Exchange-Correlation Energy Functionals: Application to the Calculation of Ionization Potentials and Electron Affinities, J.B. Krieger, Jiqiang Chen, Yan Li and G.J. Iafrate, International Journal of Quantum Chemistry (Quantum Chemistry Symposium 29, 79 1995).
- 4) Kohn-Sham Potentials for Spin Polarized Atomic Systems, Jiqiang Chen, J.B. Krieger, Y. Li, R.O. Esquivel and M.J. Stott, Bulletin of the American Physical Society 40, 142 (1995).
- 5) Capacitive Nature of Atomic Sized Structures, G.J. Iafrate, K. Hess, J.B. Krieger and M. Macucci, Physical Review B 52, 10,737 (1995).
- 6) Comparative Study of Kohn-Sham Potentials in Spin Density and Orbital Functional Theory, J.B. Krieger, Jiqiang Chen, Y. Li and G.J. Iafrate, Bulletin of the American Physical Society 40, 142 (1995).
- 7) Application of Kohn-Sham Theory for Orbital Dependent (Self-Interaction-Corrected) Exchange-Correlation Energy Functionals to Diatomic Molecules, J.B. Krieger, Jiqiang Chen and G.J. Iafrate, 6th International Conference on Density Functional Theory, Paris, August 1995.
- 8) Kohn-Sham Potentials for Spin Polarized Atomic Systems, Jiqiang Chen, J.B. Krieger, R.O. Esquivel, M.J. Stott and G.J. Iafrate, Physical Review A 54, 1910 (1996).

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- 9) Kohn-Sham Calculations with Self-Interaction-Corrected Local-Spin Density Exchange-Correlation Energy Functional for Atomic Systems, J. Chen, J.B. Krieger, Y. Li and G.J. Iafrate, Physical Review A 54, 3939 (1996).
- 10) Application of Kohn-Sham Theory for Orbital Dependent (Self-Interaction-Corrected) Exchange-Correlation Energy Functionals to First Row Heteropolar Diatomic Molecules, J.B. Krieger, Jiqiang Chen and G.J. Iafrate, Bulletin of the American Physical Society, R19-11, March 1996.
- 11) Application of Kohn-Sham Theory for Orbital Dependent (Self-Interaction-Corrected) Exchange-Correlation Energy Functionals to First Row Homopolar Diatomic Molecules, Jiqiang Chen, J.B. Krieger and G.J. Iafrate, Bulletin of the American Physical Society, R19-12, March 1996.
- 12) Simplified Accurate Approximation for the Kohn-Sham Potential using the KLI Method, J.B. Krieger, Yan Li, Yili Liu and G.J. Iafrate, International Journal of Quantum Chemistry 61, 273 (1997).
- 13) Density Functional Calculations of Ionization Potentials and Electron Affinities with a Mixing Orbital Dependent Exchange-Correlation Energy Functional, Jiqiang Chen, J.B. Krieger and G.J. Iafrate, Bulletin of the American Physical Society, 42, 572 (1997).
- 14) Kohn-Sham Theory with Exact Exchange, J.B. Krieger, Jiqiang Chen and G.J. Iafrate, Duke Symposium on Density Functional Theory (invited), June 1997.
- 15) Theoretical Determination of the Exact-Exchange Mixing Parameter, J.B. Krieger, J. Chen and G.J. Iafrate, International Journal of Quantum Chemistry (in press).
- 16) Application of Kohn-Sham Theory for Orbital Dependent (Self-Interaction-Corrected) Exchange-Correlation Energy Functionals to Diatomic Molecules, J. Chen, J.B. Krieger and G.J. Iafrate, Physical Review A (submitted for publication).
- 17) Accurate Zero Parameter Correlation Energy Functional obtained from the Homogeneous Electron Gas with an Energy Gap, J.B. Krieger, J. Chen, G.J. Iafrate and A. Savin, Bulletin of the American Physical Society, March 1998 (in press).

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- 18) Calculation of the Ionization Potentials and Electron Affinities for Atoms. J. Chen, J.B. Krieger, G.J. Iafrate and A. Savin, Bulletin of the American Physical Society, March 1998 (in press).

- 1) Scientific Personnel Supported by this project:

Professor Joseph B. Krieger-Principal Investigator

Dr. Jiqiang Chen-Post Doctoral Research Associate

Report of Inventions-None