PHYSICAL REVIEW A VOLUME 38, NUMBER 1 JULY 1, 1988

Brief Reports

Brief Reports are short papers which report on completed research which, while meeting the usual **Physical Review** *standards of scientific quality, does not warrant a regular article. (Addenda to papers previously published in the* **Physical Review** *by the same authors are included in Brief Reports.) A Brief Report may be no longer than 3½ printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Atomic correlation energy differences by means of a polarization potential

Patricio Fuentealba
Departamento de Física, Facultad de Ciencias, Universidad de Chile, Casilla Postal 653, Santiago, Chile

H. Stoll and Andreas Savin
Institut für Theoretische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-7000 Stuttgart 80, West Germany

(Received 10 November 1987)

Correlation energy differences have been evaluated using an empirical polarization potential for the two-, three-, and four-electron atom series. In contrast to local-density approximations the Z dependency of the correlation energies has been well reproduced. Moreover, the quantitative agreement with experimental values is surprisingly good. Deviations are smaller than 0.01 hartree.

There are a number of methods for calculating the correlation energy of atoms, molecules, and solids. Rigorous methods such as configuration interaction, many-body perturbation theory, coupled-pair theories, and Green's-function techniques are too expensive for many practical applications. Hence there have been many attempts to evaluate correlation energy contributions to measurable properties, e.g., ionization potentials, dissociation energies, in an approximate manner.

The density-functional method provides an economical and physically appealing alternative to more elaborate methods.[1-3] The exact density functional is not explicitly known and could be very complicated, but simple local approximations are available. For closed-shell systems the local-density approximation (LDA) gives the correlation energy as a functional of the density ρ,

$$E_c\,|\rho\,| = \int \rho(\mathbf{r})\varepsilon_c(\rho)d\mathbf{r}\ , \tag{1}$$

in which $\varepsilon_c(\rho)$ is the correlation energy per electron of a homogeneous electron gas with density $\rho(\mathbf{r})$. For atoms and molecules good results have been obtained by removing self-interaction terms and taking $\rho(\mathbf{r})$ as the Hartree-Fock density $\rho_{\mathrm{HF}}(\mathbf{r})$.[1,4,5]

However, the various LDA methods fail to reproduce the Z dependency of correlation energies for the two- and four-electron atoms. For the two-electron series He, Li^{+}, $\mathrm{Be}^{2+}, \ldots$, the correlation energies calculated by the LDA increase as $\sim \ln Z$,[4] while the exact correlation energies approach a constant value.[6] For the four-electron series Be, B^{+}, $\mathrm{C}^{2+}, \ldots$, on the other hand, the correlation energy should be linear in Z,[6] but the LDA gives a dependence of $\sim \ln Z$ again.[7]

In this Brief Report we shall show that by using an empirical approach, which is closely related to LDA methods, we are able to reproduce, in an impressive manner, the Z dependency of correlation energies for the two-, three-, and four-electron series.

Our goal is to calculate correlation energy differences,

$$\Delta E_c = E_c(N) - E_c(N-1)\ , \tag{2}$$

where N is the electron number. To do this we define a correlation energy potential which gives ΔE_c directly,

$$\Delta E_c = \int \rho_{\mathrm{HP}}(\mathbf{r}) V_c(\mathbf{r}) d\mathbf{r}\ . \tag{3}$$

The motivation and justification to define a potential $V_c(\mathbf{r})$, which is in general a nonlocal one, are found in works by Gunnarsson and Lundqvist,[8] Ros,[9] and Sharma and Thakkar.[10]

It is worthwhile to mention that Eq. (3) gives energy differences directly, i.e., physically observable magnitudes, which distinguish it from the LDA and other methods. The total correlation energy of an N-electron system can be obtained only through a consecutive application of Eq. (3) to the N-,$(N-1)$-,$(N-2)$-, ... electron systems.

In this work $V_c(\mathbf{r})$ will be approximated through an empirical polarization potential, which describes the polarization of the $(N-1)$-electron charge density due to an external electron. There is a variety of grounds to justify this approximation. Perhaps Born and Heisenberg[11] were the first to apply a polarization potential in order to understand the spectrum of alkali-metal ions. Heisenberg also used a polarization potential to calculate the excited states of helium.[12] More recently, Ros[9] computed a "correlation potential" for the two-electron atoms H^{-}, He, and Ne^{8+} from explicitly correlated wave functions.

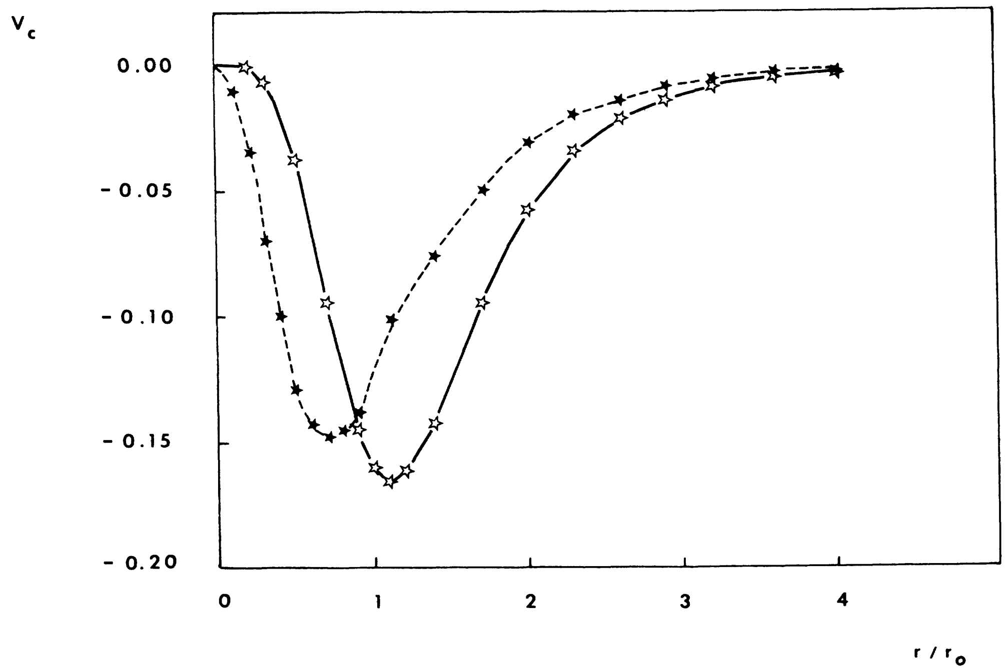

FIG. 1. Polarization potential with both cutoff functions plotted in reduced variables. Energies are in units of $\alpha/2$ and distances in units of r_0. ——, cutoff function of Müller *et al.* (Ref. 15); — — —, cutoff function of Midgalek and Baylis (Ref. 21).

After expanding the numerical values in spherical harmonics he found that the leading term was very well reproduced through a polarization potential. It is well known that the long-range correlation energy can be described by a polarization potential and efforts have been made to match it, at some radius, to more elaborate methods.[13] In a line very similar to our work, Midgalek and Baylis[14] applied a polarization potential to improve the electron affinities of halogen atoms calculated by the Hartree-Fock method. Lastly, the evaluation of core-valence correlation energies using a polarization potential is well known.[15–19] Besides the already cited works there are many other important papers in which the concept of a polarization potential has been discussed (e.g., Ref. 20).

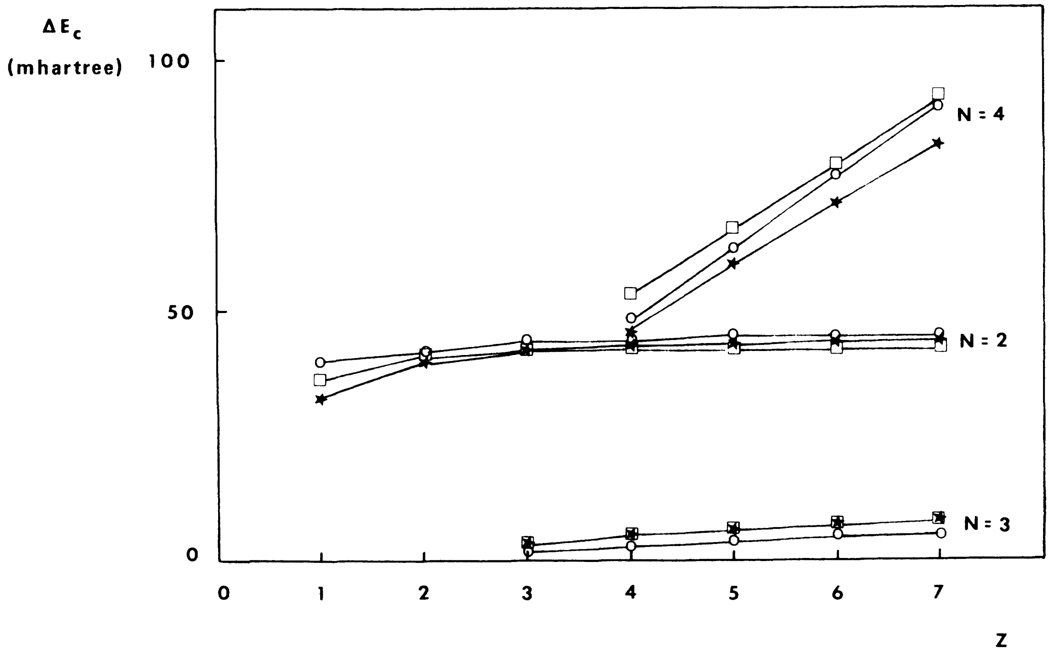

FIG. 2. Correlation energy differences for the two-, three-, and four-electron series. □, cutoff function of Müller *et al.* (Ref. 15); *, cutoff function of Midgalek and Baylis (Ref. 21); and ○, experimental values from Ref. 6.

TABLE I. Correlation energy differences $\Delta E_c = E_c(N) - E_c(N-1)$ (in mhartree). N is the electron number.

Atom	N	r_0 (a.u.)	α (a.u.)		ΔE_c	
				MB[a]	MFM[b]	Expt.[c]
H^-	2	1.5	4.5	33	36	40
He	2	0.75	0.281 25	40	41	42
Li^+	2	0.50	0.055 56	42	42	44
Be^{2+}	2	0.375	0.017 58	43	42	44
B^{3+}	2	0.30	0.007 20	43	42	45
C^{4+}	2	0.25	0.003 47	44	42	45
N^{5+}	2	0.214 29	0.001 87	44	42	45
Li	3	0.572	0.1915	3	3	2
Be^+	3	0.414	0.052	5	5	3
B^{2+}	3	0.324	0.019	6	6	4
C^{3+}	3	0.267	0.0088	7	7	5
N^{4+}	3	0.226	0.0047	8	8	5
Be	4	2.280	25.0	46	53	47
B^+	4	1.636	8.12	59	66	63
C^{2+}	4	1.279	3.59	71	79	77
N^{3+}	4	1.052	1.90	83	92	91

[a] Midgalek and Baylis cutoff function (Ref. 21).
[b] Müller *et al.* cutoff function (Ref. 15).
[c] Experimental values from Ref. 6.

The correlation potential to be used has the following form:

$$V_c(r) = -\frac{\alpha}{2r^4}\omega(r) , \tag{4}$$

where α is the electric dipole polarizability of the respective $(N-1)$-electron ion. For the cutoff function $\omega(r)$, necessary to avoid divergence as r goes to zero, two different functional forms were employed. The first one, used by Midgalek and Baylis,[14,21,22] is

$$\omega_{\text{MB}}(r) = \frac{r^6}{(r_0^2 + r^2)^3} . \tag{5}$$

The second one, proposed by Müller *et al.*[15] has the following form:

$$\omega_{\text{MFM}}(r) = (1 - e^{-r^2/r_0^2})^4 . \tag{6}$$

In both formulas the cutoff parameter r_0 was chosen as the expectation value $\langle r \rangle$ of the outermost occupied orbital.

There is no conclusive reason to prefer one cutoff function or another, and the final results depend slightly on the functional form. The same conclusion has been found in many applications of polarization potentials.[15,16,22] In Fig. 1, the polarization potential curves with both cutoff functions are shown. Although the differences between the polarization potentials appear to be large at small distances, the results of applying Eq. (3) are very insensitive to these differences. The use of a relatively simple form for the polarization potential has been well justified in many works (e.g., Refs. 15, 16, and 18). Other theoretically derived forms[23,24] cannot account for the exclusion effect; therefore it seems to be more appropriate to choose a form which is convenient for integration and which gives a clear physical picture.

To evaluate the polarization potential one needs numerical values of α for the $(N-1)$-electron ions. For the one-electron series the α values are exactly known, $\alpha = 4.5/Z^4$ (in a.u.). For the two-electron series the values were taken from Refs. 15 and 25. For the three-electron series we calculated them using a finite-field method and psuedopotentials with a large basis set. Details of the computational method can be found in Refs. 19 and 26. The Hartree-Fock density $\rho_{\text{HF}}(\mathbf{r})$ entering into Eq. (2) was taken to be the density of the outermost orbital. It was numerically obtained using the atomic Dirac-Fock program written by Desclaux.[27]

The results for the two-, three-, and four-electron series are shown in Table I and Fig. 2. In Table I, the parameters used in the polarization potential are also listed. The first observation confirms that the numerical results do not depend significantly on the specific form of the cutoff function. The calculated correlation energy differences are compared to "experimental" ones, which were computed using experimental ionization potentials and Hartree-Fock energies, using estimates for relativistic effects and radiation corrections.[6] It is seen that not only the correct trends for each series are well reproduced but also that the calculated values are quantitatively in very good agreement with the experimental ones. The deviations are smaller than 0.01 hartree. In view of these remarkable results, we conclude that it could be worthwhile to explore further the virtues of the polarization concept for estimating correlation energies.

Part of this work was supported by the Dirección de Investigación y Bibliotecas, Grant No. E-2579-8713 and the Consejo Nacional de Investigaciones Científicas y Technológicas (Project No. 634).

[1] H. Stoll and A. Savin, in *Density Functional Methods in Physics,* edited by R. Dreizler and J. da Providencia (Plenum, New York, 1986).

[2] A. S. Bamsai and B. M. Deb, Rev. Mod. Phys. **53**, 95 (1981).

[3] R. G. Parr, Ann. Rev. Phys. Chem. **34**, 631 (1983).

[4] H. Stoll, E. Golka, and H. Preuss, Theor. Chim. Acta **55**, 29 (1980).

[5] A. Savin, P. Schwerdtfeger, H. Preuss, H. Silberbach, and H. Stoll, Chem. Phys. Lett. **98**, 226 (1983).

[6] M. H. Ang, K. Yates, I. G. Csizmadia, and R. Daudel, Int. J. Quantum Chem. **20**, 793 (1980).

[7] J. P. Perdew, E. R. McMullen, and A. Zunger, Phys. Rev. A **23**, 2785 (1981).

[8] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

[9] P. Ros, Chem. Phys. **42**, 9 (1979).

[10] B. S. Sharma and A. J. Thakkar, J. Chem. Phys. **83**, 3577 (1985).

[11] M. Born and W. Heisenberg, Z. Phys. **23**, 388 (1924).

[12] W. Heisenberg, Z. Phys. **39**, 499 (1927).

[13] J. K. O'Connell and N. F. Lane, Phys. Rev. A **27**, 1893 (1983).

[14] J. Midgalek and W. E. Baylis, Phys. Rev. A **26**, 1839 (1982).

[15] W. Müller, J. Flesch, and W. Meyer, J. Chem. Phys. **80**, 3297 (1984).

[16] P. Fuentealba, Ph.D. thesis, Stuttgart University, 1984.

[17] P. Fuentealba, H. Preuss, H. Stoll, and L. v. Szentpály, Chem. Phys. Lett. **89**, 418 (1982).

[18] H. Stoll, P. Fuentealba, M. Dolg, J. Flad, L. v. Szentpály, and H. Preuss, J. Chem. Phys. **79**, 5532 (1983).

[19] P. Fuentealba, L. v. Szentapály, H. Preuss, and H. Stoll, J. Phys. B **18**, 1287 (1985).

[20] N. F. Mott and N. S. W. Massey, *The Theory of Atomic Collisions,* 3rd ed. (Oxford University Press, Oxford, 1971), and works cited therein.

[21] J. Midgalek and W. E. Baylis, J. Phys. B **11**, L497 (1978).

[22] J. Midgalek and W. E. Baylis, J. Phys. B **12**, 2595 (1979).

[23] A. Temkin, Phys. Rev. **107**, 1004 (1957).

[24] S. W. Wang, H. S. Taylor, and R. S. Yaris, Chem. Phys. **14**, 53 (1976).

[25] P. C. Schmidt, A. Weiss, and T. P. Das, Phys. Rev. B **19**, 5525 (1979).

[26] P. Fuentealba, J. Phys. B **15**, L555 (1982).

[27] J. P. Desclaux, Comput. Phys. Commun. **9**, 31 (1975).