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Relation Between the Repulsive Interaction and the Overlap of the Electron Densities†

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The relations between the repulsive interactions and the electron density overlaps are investigated for various closed shell-closed shell pairs, including the systems containing alkali and halide ions. It is found that the repulsive interaction(V_{rep}) depends on the overlap of the electron density(S_ρ) according to a simple exponential relation, $V_{\text{rep}} = \text{A}s_\rho^{\alpha}$. Furthermore, for most of the closed shell systems the α values are near unity and the A values doe not vary much. The same tests are also performed for the open shell-closed shell, and the open shell-open shell pairs. Although the results for these systems also show exponential dependences of the repulsive interactions on the density overlaps, the details of the dependence differ greatly from those for the closed shell systems and also vary widely from one individual system to another.

Introduction

Closed shell repulsive force is generally interpreted in a simple manner in terms of the Pauli exclusion principle: The principle effectively prevents overlapping of the electron densities when they come close to each other, thus leading to higher energy, the cause of the repulsion[1]. This in turn suggests that the closed-shell repulsions depend in some way on the overlap of electron densities[2].

Much work was done to understand the relation between the dominant part of the repulsion, *i.e.* the exchange repulsion, and the overlap of the wavefunctions, densities, or some other related quantities[3]. The so-called "Mulliken approximation" is an earliest example:

$$E_{\mathbf{ex}}(R) = kS^2/R, \tag{1}$$

where S is the overlap intergral at internuclear distance R producing the exchange repulsion E_{ex}[4]. Murrell and Texeira-Dias[5] proposed an alternative approximation,

$$E_{\mathbf{ex}}(R) = (a+bR) \iint \phi_a^2(1)\, r_{12}^{-1}\, \phi_b^2(2)\, d\boldsymbol{r}, \tag{2}$$

where the integral represents the overlap-dependent part of the Coulomb integral.

Several years ago one of the present authors (YSK) and coworkers checked the direct quantitative relationship between the entire repulsive interaction and the density overlap itself for the closed shell systems[6]. They performed their tests on three inert gas systems, He-He, Ne-Ne and Ar-Ar, and reported a striking result that over most of its repulsive part the interaction is approximately proportional to the overlap of the electron densities(S_ρ). Their results showed that the rough magnitudes of those closed-shell repulsive interactions depend only on the size of the density overlaps and not on the species of the interacting atoms. At a same interatomic distance the Ar-Ar interaction is more repulsive than the He-He interaction because the Ar system has a larger density overlap than does the He system; but at a same value of the density overlap the repulsive interactions of the two systems do not differ very much. More recently Nyeland and Toennies[7] used a new quantity

$$N = S_\rho / R^2, \tag{3}$$

which is the density overlap divided by the square of the internuclear distance, and found that the dependence of the repulsive potentials on N is more stable than the dependence on S_ρ for wider ranges of R for most of the inert gas systems.

In the present paper we perform the test of Ref. 6 for the closed shell systems that were not tested in the original work. In addition to the inert gas pair systems tested by Nyeland and Toennies in Ref. 7, they also include the systems involving alkali and halide ions. The results exhibit roughly the same trend found in the original work. We also check whether the test can be extended to different types of systems, namely open shell-closed shell systems and the open

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shell-open shell systems. Although these systems also show exponential dependences of the repulsive interactions on the density overlaps, the details of the dependence differ greatly from the closed shell case, and also vary widely from one individual system to another. For these systems there obviously are extra effects in addition to the electron-density overlap, and thus no simple relation can represent the dependence for all the systems.

Method

Instead of the usual overlap integral, we defined the "density overlap" S_ρ. The latter represents the direct measure of the magnitude of the overlap of the electron densities,

$$S_\rho(R) = \int \rho_A(r)\rho_B(r)\,dr. \tag{4}$$

Here, ρ_A and ρ_B are the unperturbed electron densities of the closed-shell atoms or ions A and B, and the integration is carried out over the entire space of r over which the densities are extended. S_ρ does not go to unity as R, the internuclear distance, goes to zero, because the overlap is not normalized. The atomic and ionic densities ρ were calculated from the analytic Hatree-Fock wavefunctions of Clementi and Roetti[8] for all the atoms and ions except for hydrogen atom, for which the exact wavefunctions were used. The integral in Eq. (4) was evaluated numerically from the densities thus obtained.

We then compared the repulsive interaction $V_{rep}(R)$ directly with $S_\rho(R)$ to find relationship between them. For all the systems over a considerable range of R the relationship was found to be very well represented by

$$V_{rep}(R) = AS_\rho(R)^\alpha \tag{5}$$

The numerical values of α and A were obtained from the logarithmic plots of V_{rep} *vs.* S_ρ using the linear least square method[9]. The sources of V_{rep}, chosen among the best available empirical and theoretical potentials, are given in the next sections where the detailed results for the systems are presented.

Results and Discussion

A. Inert Gas Atom-Inert Gas Atom Pairs

We checked the diatomic inert gas pairs that contain He, Ne, Ar and Kr, including the pairs already treated in Ref. 6. The repulsive potentials for all the systems except Ar-Kr were from Y. T. Lee and coworkers[10], and that for Ar-Kr, from Gough and coworkers[11]. All these potentials were obtained from the molecular beam scattering experiments.

Figure 1 shows the logarithmic plots of the repulsive interactions *vs.* the density overlaps for the systems not covered by Ref. 6. The values of a and A resulting from the linear square fits to Eq. (5), and the range of R over which the fits are satisfactory, are given in Table 1 for all the systems.

The exponents α show somewhat larger variations than that shown in Ref. 6, for which the α values stayed closer to unity for the three homogeneous diatomic pairs. The values of A, with a single exception, the Ne-Ar system, fall within the same range as were found in Ref. 6, and do not differ from one another by more than a factor of 3. The α value also shows the largest deviation for the Ne-Ar system. The reason for such an exceptional behavior in this particular case cannot be determined from the simple kind of test performed in the present work. But sine there is no reason that this particular system should behave differently from the other inert gas atom-inert gas atom pair systems, this difference suggests that there may be some problems in the Ne-Ar repulsive potential itself. Indeed, there are still wide disagreements on this potential, and it is hoped that the present work encourage further investigations on it.[12] The range of R values for all the systems generally correspond to the S_ρ values of 1-10^{-3}.

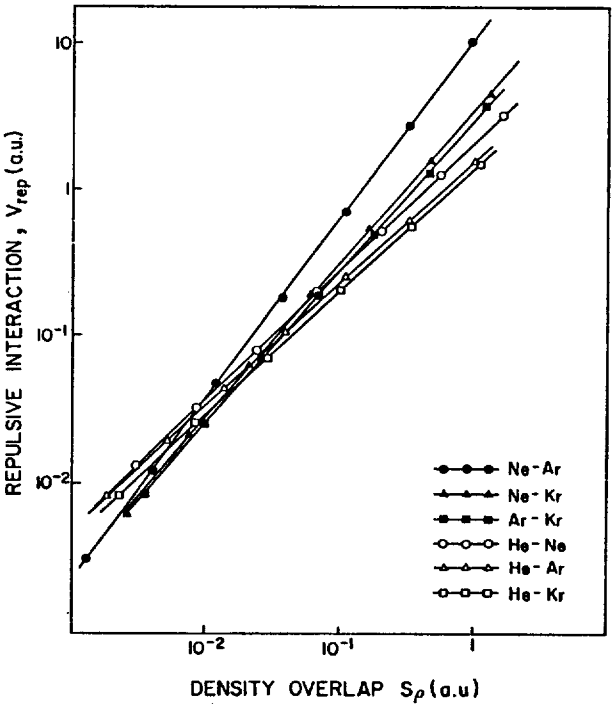

Figure 1. Inert gas diatomic pairs.

Table 1. Results for the Inert Gas Diatomic Pairs. All Values are Given in Atomic Units

	He-He*	He-Ne	He-Ar	He-Kr	
α	0.99	0.837	0.878	0.836	
A	3.55	1.421	2.097	1.617	
Range	1.0-4.5	1.0-3.5	1.0-4.5	1.5-4.5	
	Ne-Ne*	Ne-Ar	Ne-Kr	Ar-Ar*	Ar-Kr
α	0.98	1.254	1.050	0.96	1.026
A	3.16	12.138	3.543	2.24	3.086
Range	1.0-4.5	1.0-5.0	2.0-5.0	1.0-5.5	2.5-5.5

* from reference 6.

B. Closed Shell Ion-Inert Gas Atom Pairs

Since the alkali ions and the halide ions are also of the closed shell electronic structure, we checked the pairs made of one of such ions and an inert gas atom. The ions included are Li^+, Na^+, K^+, Cl^-, and Br^-. The repulsive potentials used are those obtained from the scattering experiments by Inouye and coworkers[13].

The results are very similar to the case of the inert gas diatomic pairs. As Table 2 shows, for the entire ranges of R

Table 2. Results for Closed Shell Ion-Inert Gas Atom Pairs. All Values are Given in Atomic Units

	Li^+-He	Li^+-Ne	Li^+-Ar	Na^+-He	Na^+-Ne	
α	0.952	0.919	0.975	0.950	0.932	
A	4.087	3.115	4.634	2.562	2.373	
Range*	1.48-2.29	1.89-2.83	2.46-3.59	1.98-2.82	2.49-3.31	
	Na^+-Ar	Na^+-Kr	K^+-He	K^+-Ne	K^+-Ar	K^+-Kr
α	1.087	1.091	0.921	0.918	0.848	0.951
A	3.556	3.307	2.278	1.829	1.582	1.865
Range*	3.08-3.97	3.23-4.20	2.32-3.34	2.93-3.86	3.38-4.59	3.63-4.78
	Cl^--He	Cl^--Ne	Cl^--Ar	Br^--He	Br^--Ne	Br^--Ar
α	0.862	0.926	0.965	0.880	0.968	0.910
A	1.898	1.447	1.387	2.023	1.434	1.205
Range*	2.36-3.82	2.95-4.29	3.42-4.80	2.57-4.03	3.16-4.52	3.65-5.12

* These range are the ranges over which the potential data are available.

Table 3. Results for Closed Shell Ion-Closed Shell Ion Pairs. All Values are Given in Atomic Units

	Na^+-Cl^-	K^+-Cl^-
α	1.114	1.308
A	1.749	1.033
Range	0.5-2.0	1.5-2.5

Table 4. Results for Alkali Atom-Inert Gas Atom Pairs. All Values are Given in Atomic Units

	Li-He	Li-Ne	Li-Kr	Na-Ar	K-Ne	K-Ar	K-Kr
α	1.256	1.452	1.360	1.261	1.627	1.642	1.718
A	40.77	19.48	7.433	3.155	25.84	19.16	11.23
Range	3.0-9.0	3.0-7.5	3.0-6.5	4.6-6.0	4.4-6.0	5.2-7.0	5.5-7.0

over which the potential data are available, both the α values and the A values fall well within the range found in the diatomic pairs, with no exceptional case as that of the Ne-Ar pair.

C. Closed Shell Ion-Closed Shell Ion Pairs

Alkali halide molecules are known to be formed of an alkali ion and a halide ion, both of which are of the closed shell electronic structure. We checked two cases, NaCl and KCl, using the electron-gas model potential data of Gordon and Kim[14], after eliminating the Coulombic contributions, The results, as shown in Table 3, are not very different from the other closed shell systems, but the large α values for these ionic systems imply some extra physical effects that are absent in the other systems.

Extension to the Open Shell Systems

We extended our check to the pairs containing open shell structure. Such systems can be divided into two types: open shell-closed shell systems and open shell-open shell systems. Of course the repulsive interactions for these new types of systems involve additional physical effects that are absent in the closed shell repulsive interactions. It is thus difficult to expect the results either to be so simple or to bring much physical insight into the nature of the open shell repulsive forces. But nevertheless, it would be worthwhile to show how the results for these two types of systems are different -both from the closed shell systems and from each other.

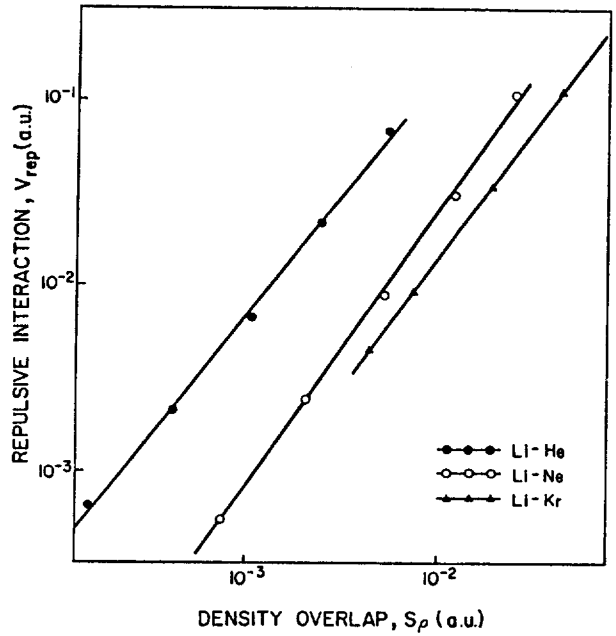

Figure 2. Li-inert gas atom pairs.

A. Open Shell-Closed Shell Systems

The repulsive potentials for this type of systems are available for several alkali atom-inert gas atom interactions from the scattering experiments of Dehmer and Wharton[15] and of Malerich and Cross[16].

The results are summarized in Table 4 and are plotted in Figures 2 and 3. The repulsive interactions for the systems also show exponential dependence of Eq. (5), but the values of α are generally larger than those for the closed shell-closed shell systems. This difference must be from the effect of the open shell electrons of the alkali atoms. The A values are also larger than those for the closed shell-closed shell pairs. Among the pairs containing a common alkali atom the α values do not vary much, but those with heavier inert gas atom have lower A values and thus lower repulsive interactions at a same density overlap.

B. Open Shell-Open Shell Systems

The systems that we studied include the dialkalis (Li-Li, Na-Na), the alkali hydrides (Li-H, Na-H), the hydrogen halides (H-F, H-Cl, H-Br) and the dihalides (Cl-Cl, Br-Br), as well

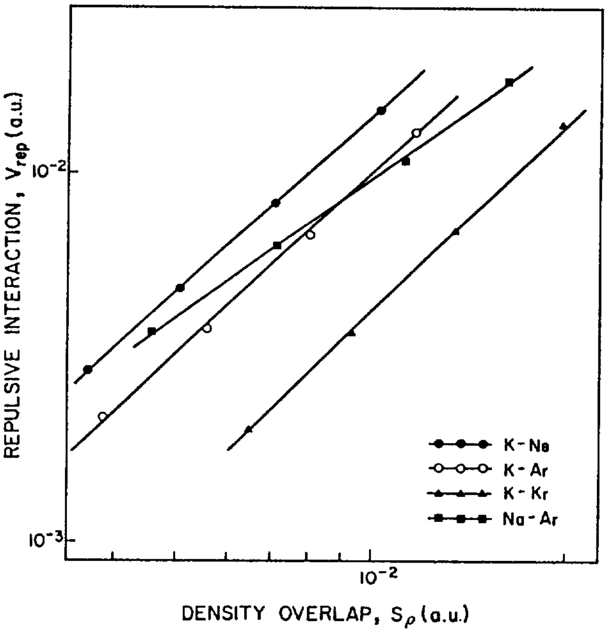

Figure 3. Na-inert gas atom pairs and K-inert gas atom pairs.

Table 5. Results for Open Shell-Open Shell Systems. All Values are Given in Atomic Units

	H-H	Li-Li	Na-Na	Li-H	Na-H	H-F
α	12.03	0.07377	0.4875	0.7442	1.556	4.013
A	2.058×10^{17}	0.1095	1.067	4.251	7.312	48.39
Range	0.4-0.65	0.4-1.4	0.6-2.1	0.3-0.9	0.6-1.8	0.2-0.9
	H-Cl	H-Br	Cl-Cl	Br-Br	N-N	O-O
α	2.388	2.095	2.369	2.363	4.280	2.799
A	8.782	2.075	4.717	0.8414	1.253	0.593
Range	0.3-1.3	0.5-1.5	1.0-2.8	1.5-3.0	0.6-1.4	0.5-1.5

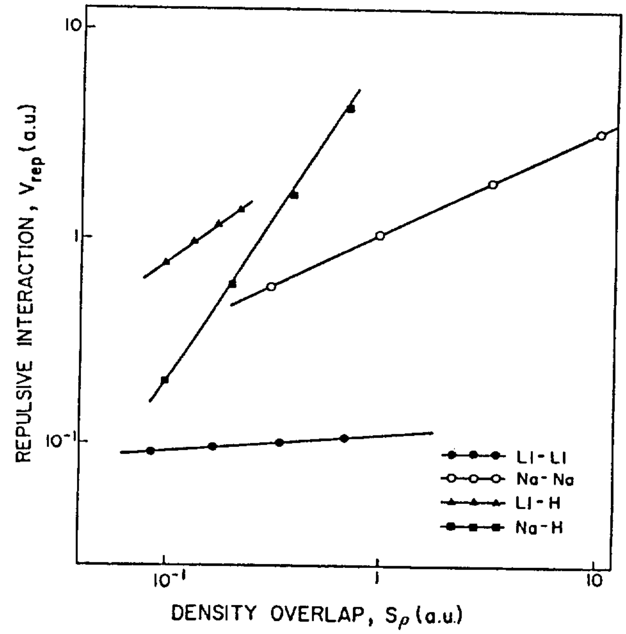

Figure 4. Dialkalis and Alkalihalides.

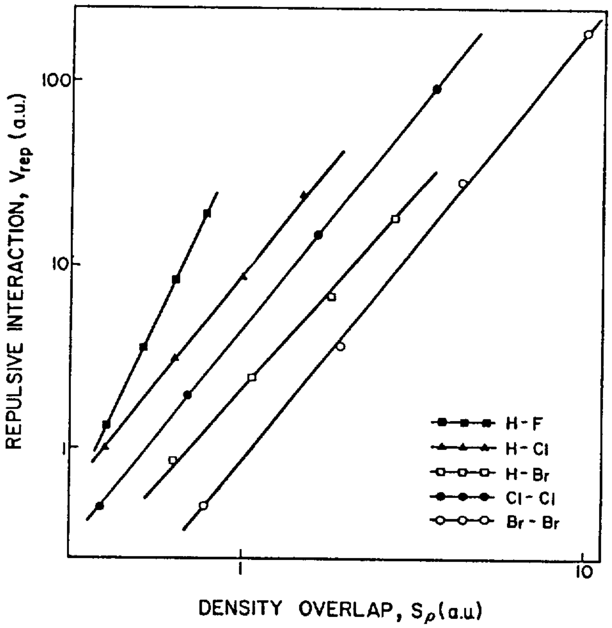

Figure 5. Hydrogen halides and Dihalides.

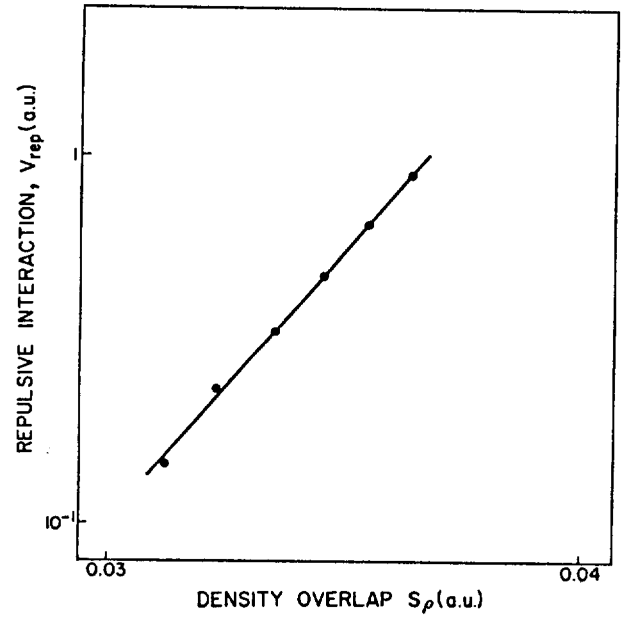

Figure 6. H_2 molecule.

as the hydrogen, nitrogen and oxygen molecules (H-H, N-N, O-O). The repulsive potentials were obtained from the *ab-initio* calculation of Kolos and Wolniewicz for the hydrogen molecule[17] and from the spectroscopic data by Stwalley and coworkers for the other systems[18].

The results are summarized in Table 5 and are plotted in Figures 4-7. Although the repulsive interaction for each system could be fitted to Eq. (5), the α and A values show a great viriation both from the earlier types of the systems and among the open shell-open shell systems themselves. This doubtless reflects the various effects taking place when the open shell electron clouds approach each other, which lead to the formation of chemical bonds at larger distances, and which no simple equation like Eq. (5) can represent. Among these open shell-open shell systems, the α values are the

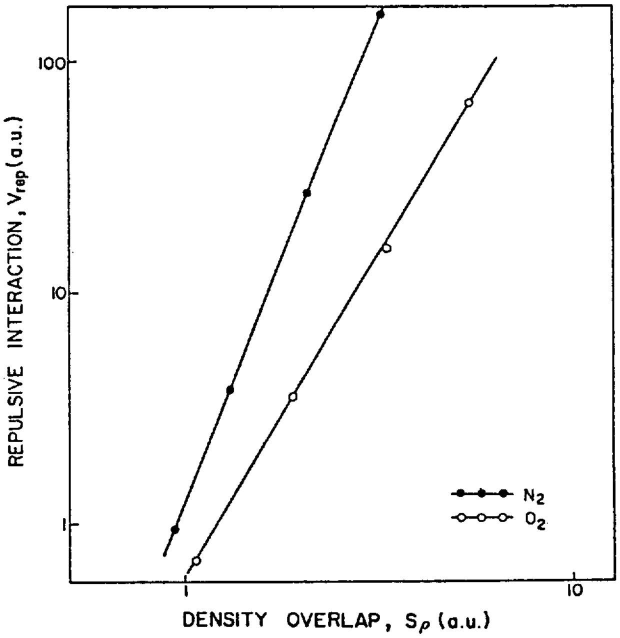

Figure 7. N_2, O_2 molecules.

smallest for the dialkali pairs, somewhat larger for the alkali hydrides, and still larger, falling within the range of 2-5, for the other molecules treated except for the hydrogen molecule. For the hydrogen repulsion, the values of both α and A are much greater than those of the other systems.

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