

Barrier for the reaction $X_{20}^+ + X_{20}^+ \rightarrow X_{40}^{2+}$ in alkali-metal clusters related to electron density at the bond midpoint of the supermolecule $(X_{20}^+)_2$

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Using the extended Thomas-Fermi version of density-functional theory (DFT), calculations are presented for the barrier for the reaction $\text{Na}_{20}^+ + \text{Na}_{20}^+ \rightarrow \text{Na}_{40}^{2+}$. The deviation from the simple Coulomb barrier is shown to be proportional to the electron density at the bond midpoint of the supermolecule $(\text{Na}_{20}^+)_2$. An extension of conventional quantum-chemical studies of homonuclear diatomic molecular ions is then effected to apply to the supermolecular ions of the alkali metals. This then allows the Na results to be utilized to make semiquantitative predictions of position and height of the maximum of the fusion barrier for other alkali clusters. These predictions are confirmed by means of similar DFT calculations for the K clusters.

I. INTRODUCTION

Sattler *et al.*¹ found experimentally that Coulomb repulsion in multiply charged clusters may result in fission into fragments with smaller charges: the so-called Coulomb explosion. Since that time, work by several groups has helped a lot in clarifying the nature of the Coulomb explosion.²⁻⁴ In earlier work,⁵ a combination of density-functional theory (DFT) and the jellium model has been employed to study some specific fission channels for doubly charged clusters. A key aspect to understand charged-cluster fission is that this is a barrier-controlled process.

The present work is concerned solely with symmetric fission. As a specific example we consider the fission of Na_{40}^{2+} into $\text{Na}_{20}^+ + \text{Na}_{20}^+$. Our intention is to analyze the fission barrier. However, for reasons which will become clear below, it is more convenient to focus on the opposite process in which two Na_{20}^+ clusters fuse to form Na_{40}^{2+} . In other words, we consider the barrier for the fusion of two singly charged identical clusters. Using the same model as in Ref. 5, calculations will first be presented of the deviation, $\Delta(R)$ say, between the barrier preventing the fusion of $\text{Na}_{20}^+ + \text{Na}_{20}^+$ into Na_{40}^{2+} and the simple Coulomb barrier e^2/R . (R indicates the separation between the centers of the two Na_{20}^+ clusters.) These results are then analyzed, using recent progress in the quantum chemistry of homonuclear diatomic molecules, in terms of the electron density, $\rho_m(R)$ say, at the midpoint of the bond⁶⁻⁸ in the supermolecule $(\text{Na}_{20}^+)_2$ at

separation R . It is found that $\Delta(R)$ is proportional to $\rho_m(R)$ over a substantial range of cluster separation R .

Motivated by the success for the $(\text{Na}_{20}^+)_2$ supermolecular ion of arguments paralleling those of conventional quantum chemistry, an extension of the work of Laurenzi⁹ is proposed for predicting semiquantitatively the displacement of the maximum, and indirectly also the height, of the fusion barrier for the reaction $\text{K}_{20}^+ + \text{K}_{20}^+ \rightarrow \text{K}_{40}^{2+}$ (and similar reactions for other alkali elements) from that of the sodium case. These predictions are then tested by direct DFT calculations on the K system.

Symmetric cluster fusion has also been studied by Schmidt and co-workers^{10,11} and by Saito and Ohnishi.¹² These authors, however, were interested in the fusion of colliding neutral clusters, in which case the primary quantity of interest in our work, namely the Coulomb-derived fusion barrier, is absent.

II. DEVIATION OF FUSION BARRIER FROM SIMPLE COULOMB BARRIER DUE TO CHEMICAL BONDING IN $(\text{Na}_{20}^+)_2$

We calculate the energy of the supermolecular ion $(\text{Na}_{20}^+)_2$ using the density-functional formalism and the jellium-background model.^{5,13} The positive ionic background of each Na_{20}^+ cluster is assumed to be a spherical jellium (with constant positive density) of radius $R = r_s N^{1/3}$ where $N=20$ and r_s , the usual electron density parameter, is equal to 4 a.u. At moderate separations

R between the centers of the two clusters the electronic cloud is shared by the two components of the supermolecule. This bonding cloud lowers a little the fusion barrier compared to the purely Coulombic barrier.

For the energy we have used an extended Thomas-Fermi approximation, namely,

$$E[\rho] = T + U_{ee} + U_{je} + U_{jj} + E_{xc} . \quad (1)$$

T is the kinetic energy of the electronic cloud, given as the sum of the local Thomas-Fermi term and the lowest-order density gradient correction (Hartree atomic units are used throughout the paper)

$$T[\rho] = \int d^3r \left[c_k \rho^{5/3} + \frac{\lambda}{8} \frac{(\nabla\rho)^2}{\rho} \right] , \quad (2)$$

with $c_k = \frac{3}{10}(3\pi^2)^{2/3}$. U_{ee} is the classical electrostatic energy of the electrons,

$$U_{ee} = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^2r d^3r' ,$$

U_{je} is the electrostatic interaction between the electrons and the positive jellium background, U_{jj} is the self-interaction of the jellium background, and finally $E_{xc}[\rho]$ is the sum of the exchange and correlation energies of the electrons. For this term we have used a local-density approximation; the exchange part is the standard Dirac term⁸ and Wigner's interpolation formula has been used for the correlation energy.¹⁴ $\rho(\mathbf{r})$ in the above expressions is the electron density distribution, and the value of the constant λ in Eq. (2) will be discussed later.

For a given separation R between the two Na_{20}^+ clusters, the minimization of $E[\rho]$ of Eq. (1) with respect to the density, subject to normalization of the density, leads to an Euler-Lagrange equation which expresses the constancy of the chemical potential $\mu(R)$ through space:

$$\mu(R) = \frac{5}{3} c_k \{ \rho(\mathbf{r}; R) \}^{2/3} + \frac{\lambda}{8} \frac{(\nabla\rho)^2}{\rho^2} - \frac{\lambda}{4} \frac{\nabla^2\rho}{\rho} + V(\mathbf{r}; R) . \quad (3)$$

As emphasized in Ref. 6, this equation relates $\mu(R)$, in particular, to the bond midpoint electron density $\rho(0; R) \equiv \rho_m^*(R)$ and its derivatives $\nabla\rho$ and $\nabla^2\rho$ at the same point, plus the electrostatic potential $V_{es}(0; R)$, which is one part of $V(\mathbf{r}; R)|_{\mathbf{r}=0}$ in Eq. (3). The other part, the exchange-correlation potential V_{xc} is taken in a local-density approximation,⁵ and hence is again determined solely by the bond midpoint density. The notation above indicates that we take the origin of coordinates at the bond midpoint. It is useful to notice that our model has axial symmetry around the bond axis.

Integrating the Euler equation (3) (the interested reader should consult Ref. 5 for full details) we have calculated the energy of the supermolecular ion $(\text{Na}_{20}^+)_2$ as a function of separation R . The results for the fusion barrier $B^{\text{fu}}(R)$ of the process $\text{Na}_{20}^+ + \text{Na}_{20}^+ \rightarrow \text{Na}_{40}^{2+}$ (using $\lambda=0.5$) have been plotted in Fig. 1, where the zero of energies is the energy of the two Na_{20}^+ clusters at infinite separation. The point of closest approach calculated in

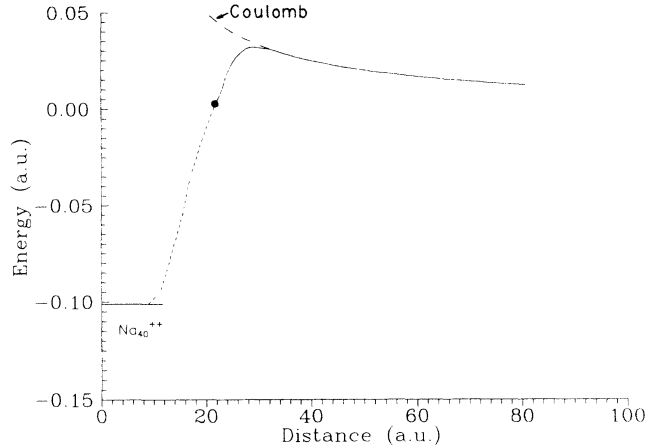


FIG. 1. Barrier for the fusion reaction $\text{Na}_{20}^+ + \text{Na}_{20}^+ \rightarrow \text{Na}_{40}^{2+}$. The zero of energies is the energy of the two Na_{20}^+ clusters at infinite separation. The pure Coulomb interaction is also plotted for comparison.

our model corresponds to the configuration in which the positive jellium backgrounds of the two Na_{20}^+ clusters just touch each other. This point is indicated by the \bullet symbol in Fig. 1. This circle has been smoothly joined by a dashed line to the energy of the fused cluster Na_{40}^{2+} , which is plotted on the left-hand side.

The pure Coulomb barrier e^2/R , obtained if the two Na_{20}^+ clusters interact like point charges, is also plotted in the figure. We observe that the true fusion barrier deviates more and more from the Coulomb barrier as the separation R decreases. We have calculated the deviation ΔR of the fusion barrier from the Coulomb barrier. The results presented in Fig. 2 show this deviation plotted against the integrated midpoint density ρ_m^* . We define ρ_m^* by

$$\rho_m^* = \int \int \rho(x, y, z=0) dx dy , \quad (4)$$

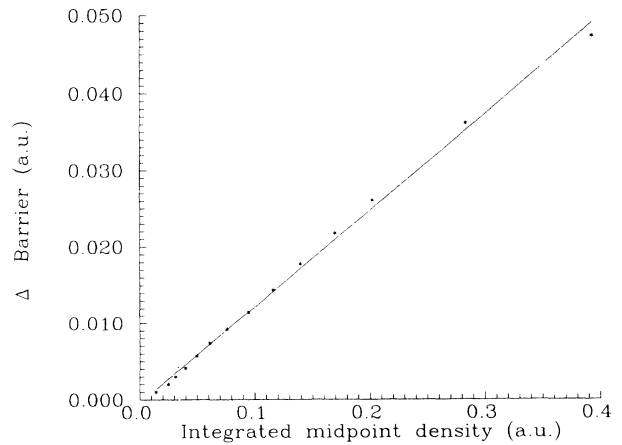


FIG. 2. Deviation $\Delta(R)$ of fusion barrier for $\text{Na}_{20}^+ + \text{Na}_{20}^+ \rightarrow \text{Na}_{40}^{2+}$ with respect to Coulomb barrier versus the bond midpoint density ρ_m^* . With the origin at the middle of the line joining the centers of the two fragments and z along the bond axis, ρ_m^* is specifically given by the integral in Eq. (4) of the text.

that is, we integrate the density over the perpendicular plane bisecting the bond axis of the supermolecular ion $(\text{Na}_{20}^+)_2$. There is a striking proportionality between $\Delta(R)$ and ρ_m^* , which is well represented by the straight line through the origin

$$\Delta = 0.139\rho_m^* . \quad (5)$$

The value $\lambda = 0.5$ in the density gradient term has been empirically found to be appropriate for describing some properties of simple metal clusters,¹⁵ as well as to fit the total energy of free atoms.¹⁶ Though it has not been done in the same detail as for $\lambda = 0.5$, the case $\lambda = 1$ has also been explored. λ is the original value proposed by von Weizsäcker¹⁷ and gives a correct description of the electron density in the "tail" region of a finite system (atom, molecule, or cluster). The slope in Eq. (5) is found to be very insensitive to λ , the estimated slope for $\lambda = 1$ being 0.143. Due to the insensitivity of Eq. (5) to λ we anticipate that this equation will be a result of some generality.

Only $\rho_m^*(R)$ appears in Eq. (5), but nevertheless it is tempting to suppose that the basic origin of the very simple result (5) must lie in the chemical potential Eq. (3) used at the bond midpoint $r = 0$. We have checked therefore that $\Delta(R)$ correlates with $\mu(R) - \mu(\infty)$, but we have not plotted the results, since Fig. 2 and Eq. (5) represent a more practical correlation.

In conventional diatomic molecules, the binding-energy curve has a minimum at intermediate interatomic separations which gives the equilibrium separation between the two atoms forming the molecule. In the supermolecular ion $(\text{Na}_{20}^+)_2$ we also have this bonding contribution, which leads to the deviation $\Delta(R)$ of the fusion barrier from the pure repulsive Coulomb interaction e^2/R . It is, in fact, this bonding term that is responsible for keeping the height of the fusion barrier finite.

III. EXTRAPOLATION OF CONVENTIONAL QUANTUM CHEMISTRY TO PREDICT THE POSITION AND HEIGHT OF THE FUSION-BARRIER MAXIMUM THROUGH THE ALKALI-METAL SERIES

From the fusion barrier for the reaction $\text{Na}_{20}^+ + \text{Na}_{20}^+ \rightarrow \text{Na}_{40}^{2+}$, plotted in Fig. 1, we see that the position of the maximum is given by a separation $R_e = 28.71$ a.u. between the centers of the two Na_{20}^+ ions, while the maximum height $B^{\text{fu}}(R_e) = B_e^{\text{fu}}$ is 0.032 a.u. The aim of the argument below is to attempt, from these results for Na, to predict the way in which R_e and B_e^{fu} will vary through the alkali-metal series Na, K, Rb, and Cs.

A. Conventional quantum chemistry for homonuclear diatomic molecular ions

Let us start from known results in conventional quantum-chemical systems which are isoelectronic, with N the fixed number of electrons. If R_e now represents the minimum in the total molecular energy $E(R)$, then

$$\left(\frac{dE}{dR} \right)_{R_e} = 0 \quad (6)$$

formally defines R_e . Then the work of Laurenzi⁹ leads to the (formally) exact result, for a diatomic molecule built from atoms of atomic number Z ,

$$\left(\frac{\partial R_e}{\partial Z} \right)_N = -\frac{R_e}{Z} + \frac{cZ}{R_e^2 E^{(2)}} . \quad (7)$$

Here $E^{(2)}$ is the force constant. The remaining quantity c in Eq. (7) is given by:⁹

$$c = 1 + \frac{R_e^2}{Z^2} \left[\frac{\partial \Phi}{\partial R} \right]_{R_e} \quad (8)$$

where

$$\Phi = \langle U_{ee}(Z, R) \rangle - \langle U_{ee}(\text{atom 1}) \rangle - \langle U_{ee}(\text{atom 2}) \rangle . \quad (9)$$

Here U_{ee} is the electron-electron interaction energy, whose exact calculation is equivalent to the complete solution of the many-electron problem. Obviously approximations are therefore necessary in this term. By means of Thomas-Fermi-like approximations, Laurenzi argues that the second term on the rhs of Eq. (7) correlates strongly with the first term, and indeed cancels two-thirds of it, to yield the result

$$\left(\frac{\partial R_e}{\partial Z} \right)_N = -\frac{1}{3} \frac{R_e}{Z} . \quad (10)$$

Unfortunately, although N_2 is a strongly bound molecule, its isoelectronic homonuclear molecular ions in the periodic table, namely C_2^{2-} and O_2^{2+} , are unbound. Thus a direct test of the usefulness of the approximate result (10) is still lacking in conventional quantum-chemical systems.

B. Heuristic generalization of Eq. (10) to supermolecular ions

In the model of Ref. 5, for given size N , the saddle point R_e of the fusion barrier leading to X_N^{2+} depends only on the metal species, characterized by the jellium density ρ_+ , which is usefully expressed in terms of the customary length r_s by

$$\rho_+ = 3/4\pi r_s^3 . \quad (11)$$

As one goes from Na to Cs, r_s varies from 4 to 5.7 a.u., representing a substantial density variation by a factor greater than 2. Nevertheless, it is tempting to ask whether, from the results for the fusion barrier for the reaction $\text{Na}_{20}^+ + \text{Na}_{20}^+ \rightarrow \text{Na}_{40}^{2+}$ described in Sec. II, one can make approximate predictions of the trends of R_e and the barrier height through the alkali-metal series.

Using the jellium model, it is ρ_+ itself that is playing here the role of the atomic number Z . This suggests immediately the heuristic generalization of the approximate quantum-chemical Eq. (10) to read

$$\frac{\partial R_e}{\partial \rho_+} = -\frac{1}{3} \frac{R_e}{\rho_+} . \quad (12)$$

In the Appendix, a model employed earlier¹⁸ is used to

regain Eq. (12) directly, without the need to rewrite Eq. (10).

Equation (12) makes the qualitative prediction that as one considers a decrease in ρ_+ from Na towards K, the position of the maximum of the barrier for symmetric fusion will move to larger R_e . Since this means that the true fusion barrier will deviate from the Coulomb barrier at larger R for K than for Na, one is led to anticipate that the fusion-barrier height will be reduced in going from Na to K.

C. Test of predictions for $\text{K}_{20}^+ + \text{K}_{20}^+ \rightarrow \text{K}_{40}^{2+}$

Integrating Eq. (12) we obtain

$$R_e = A\rho_+^{-1/3}. \quad (13)$$

In Fig. 3 we have plotted this function. The constant A was fixed by requiring that the function passes through the point corresponding to Na: $R_e = 28.71$ a.u., $\rho_+ = 0.00373$ a.u. This point is explicitly marked on the curve. The curve can be used to predict R_e for the reaction $\text{K}_{20}^+ + \text{K}_{20}^+ \rightarrow \text{K}_{40}^{2+}$, in which case $\rho_+ = 0.00216$ a.u. The predicted separation is $R_e = 34.3$ a.u. A similar calculation for Rb and Cs gives $R_e = 38.05$ a.u. and $R_e = 40.8$ a.u. respectively.

To test the validity of Eq. (12) we have performed a density-functional calculation of the barrier for the fusion reaction in the K case. The results have been plotted in Fig. 4. The barrier maximum occurs at $R = 35.38$ a.u., which agrees reasonably well with the predicted value from Eq. (13).

The qualitative prediction of Eq. (A6) of the Appendix has also been tested. This equation predicts a decrease of the height of the fusion barrier from Na to K. This is, indeed, the result of the density-functional calculation: a decrease of $B^{\text{fu}}(R_e)$ from 0.032 to 0.028 a.u.

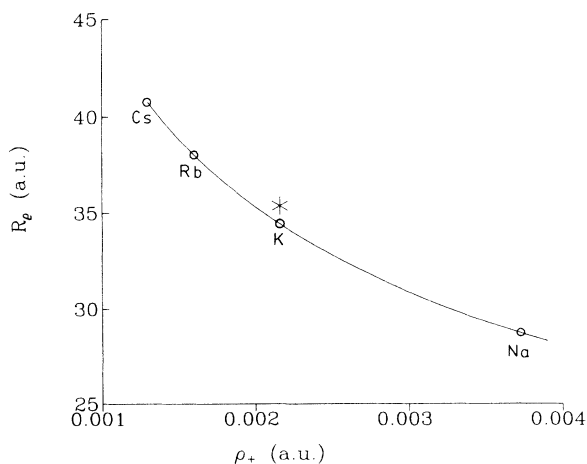


FIG. 3. Position of the maximum of the barrier for symmetric fusion of two X_{20}^+ clusters versus jellium density obtained from Eq. (12) with the boundary condition corresponding to sodium ($R_e = 28.71$ a.u. $\rho_+ = 0.00373$ a.u.). The predicted value for potassium is compared to the value calculated from density-functional theory (star).

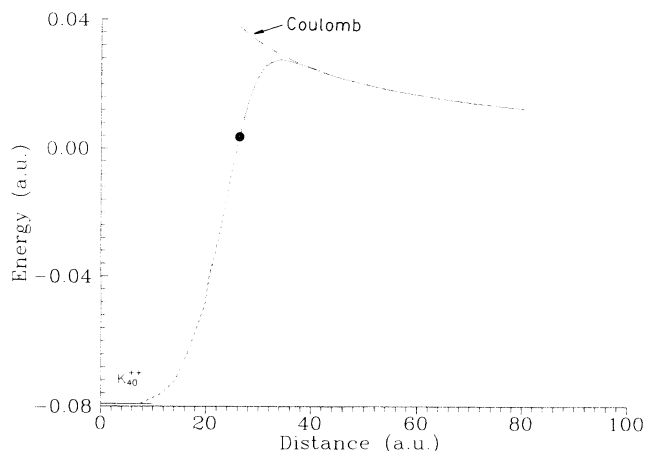


FIG. 4. Barrier for the fusion reaction $\text{K}_{20}^+ + \text{K}_{20}^+ \rightarrow \text{K}_{40}^{2+}$. The pure Coulomb interaction is also plotted for comparison.

IV. SUMMARY AND CONCLUSIONS

The main findings of the present paper are as follows:

(i) The deviation $\Delta(R)$ of the fusion barrier for the reaction $\text{Na}_{20}^+ + \text{N}_{20}^+ \rightarrow \text{Na}_{40}^{2+}$ from the simple Coulomb barrier correlates linearly, and to high accuracy, with the integrated bond midpoint electron density ρ_m^* of the supermolecule over a substantial range of cluster separation R .

(ii) The slope of Δ versus ρ_m^* is insensitive to the strength λ of the von Weizsäcker inhomogeneity kinetic-energy contribution in the DFT employed. This suggests that this correlation should be robust against refined DFT calculations.

(iii) The quantum-chemical result (10) for homonuclear diatomics has the analogue proposed in Eq. (12) for the position R_e of the fusion-barrier maximum. This correctly predicts the trend in R_e as the jellium density ρ_+ changes from the value for Na to that for K.

(iv) As an indirect consequence of (iii) above, the barrier height decreases as one goes from Na to K: this has been confirmed by performing DFT calculations of the reaction $\text{K}_{20}^+ + \text{K}_{20}^+ \rightarrow \text{K}_{40}^{2+}$.

It should be interesting to test the correlations revealed in this paper within full DFT, that is, solving the Kohn-Sham equations. Two new effects would appear in such a case that could somewhat affect the present results. One is the occurrence of electronic-shell effects which led to magic numbers of stability.¹³ The second, which is a consequence of the former, is the existence of intrinsic deformations of the jellium background for clusters with open electronic shells.¹⁹

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APPENDIX: ELEMENTARY JELLIUM MODEL FOR PREDICTING THE POSITION OF THE MAXIMUM OF THE BARRIER FOR SYMMETRIC FUSION

A simple model emerging from an earlier study by Alonso *et al.*¹⁸ is that the approximate position R_e of the maximum of the fission barrier height of doubly charged alkali-metal clusters is reached when the jellium spheres of the two fragments, of radii R_1 and R_2 respectively, just touch each other, that is, $R_e \simeq R_1 + R_2$. This conclusion, nevertheless, referred to fission (and fusion) through the most asymmetric channel,²⁰ namely $X_N^{2+} \rightleftharpoons X_{N-1}^+ + X^+$, which was the only channel studied in Ref. 18. We assume here that the same conclusion applies to the symmetric fusion channel, that is, $R_e \simeq 2R_1$. To relate to Eq. (12), one wishes therefore to write R_1 in terms of the jellium density ρ_+ . For a sphere of radius R_1 , with $(N/2) \equiv n$ atoms, one has

$$\frac{4}{3}\pi R_1^3 = n \frac{4}{3}\pi r_s^3 = \frac{n}{\rho_+}. \quad (\text{A1})$$

Hence

$$R_e = 2R_1 = 2 \left(\frac{3n}{4\pi} \right)^{1/3} \rho_+^{-1/3} \quad (\text{A2})$$

and

$$\frac{\partial R_e}{\partial \rho_+} = -\frac{1}{3} \frac{R_e}{\rho_+}, \quad (\text{A3})$$

leading back precisely to Eq. (12). In summary, Eq. (12) is exact for the simplified model in which $R_e = 2R_1$. Of course, our objective in Sec. III C is to test the validity of Eq. (12) for the extended Thomas-Fermi calculation of the barrier.

In this same model, that is for $R \simeq R_1 + R_1$, one can write for the maximum height of the fusion barrier¹⁸

$$B_e^{\text{fu}} \lesssim e^2/R_e, \quad (\text{A4})$$

though this inequality is less useful than the result (12) or equivalently (A3). If, however, we again press the question of the movement of B_e^{fu} as ρ_+ is decreased from Na_{40}^{2+} to K_{40}^{2+} , one can write, using Eq. (A4),

$$\frac{\partial B_e^{\text{fu}}}{\partial \rho_+} \simeq \frac{e^2}{R_e^2} \frac{\partial R_e}{\partial \rho_+} \quad (\text{A5})$$

and using now (A3) one arrives at

$$\frac{\partial B_e^{\text{fu}}}{\partial \rho_+} \simeq \frac{e^2}{3R_e \rho_+} \simeq \frac{1}{3} \frac{B_e^{\text{fu}}}{\rho_+}, \quad (\text{A6})$$

showing again the qualitative behavior to be expected, namely for B_e^{fu} to decrease as ρ_+ decreases from Na through Cs.

Because the argument above is based on what is essentially the inequality (A4), we stress that Eq. (A6) is not as reliable as Eq. (12). However, it is still worth noting the parallel with conventional quantum chemistry. Here, if we think of the dissociation energy of the strongly bound molecule N_2 referred to already, and consider isoelectronic sequences in which the atomic number Z ($=7$ in the example) is changed by dZ , then the dissociation energy D_e varies according to:⁹

$$\frac{dD_e}{dZ} = \frac{2D_e}{Z} - \frac{Z}{R} + \frac{\Phi}{Z}, \quad (\text{A7})$$

where Φ is defined in Eq. (9). Again, therefore, it is tempting to suppose, as with the corresponding result (7) for the equilibrium bond length, that there is a significant cancellation between the individual terms in the rhs of Eq. (A7), leading to a final result $\simeq (\frac{1}{3})D_e/Z$. However, to our knowledge, this last approximation has not been verified as a useful approximation in conventional quantum-chemical systems. As stressed already, Φ is a genuine many-electron quantity and will no doubt have to be approximated for a long time to come.

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²⁰Figure 1 shows that R_e and $2R_1$ are near 29 and 21 a.u., respectively, so the simple relation $R_e \simeq R_1 + R_1$ appears to be less accurate than for the asymmetric case.