

An SCF- $X\alpha$ -SW Study of the Ionic and Covalent State in the NaCl System

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The reference level of the separated constituents and the crossing of the potential curves for the ionic and covalent state are discussed with respect to the choice of orbital occupation numbers and Fermi-Dirac statistics. Calculations show a distinct crossing of potentials curves, when using a constraint of integer occupation numbers. No crossing is predicted, when fractional occupation numbers are used, which are adjusted according to Fermi-Dirac statistics.

Key words: SCF- $X\alpha$ -scattered wave method – NaCl – Statistical exchange

1. Introduction

In recent years the SCF- $X\alpha$ -SW-method [1] has been applied to a great variety of chemically interesting systems, mostly in connection with the interpretation of photo electron spectra. But it has also been used for calculations of molecular total energies. In particular, the problem of the dissociation limit is of considerable interest, because potential surfaces are valuable tools for describing chemical binding and because the limiting behaviour is different for the HF and SW method.

For homonuclear diatomic molecules the correct dissociation properties within the SW-method have been exemplified for some typical cases [2], including detailed discussions on the effect of the exchange parameters [3] as well as non-muffin-tin terms [4]. For heteroatomic molecules, however, the problem is more difficult to understand, since the $X\alpha$ -model of exchange obeys rigorously Fermi-Dirac statistics [5, 6]. Therefore the problem of the reference level of the separated constituents has to be discussed rather carefully.

In the present paper the well-known case of the dissociation of the NaCl system is investigated with respect to this particular aspect of the SW-method. In the neighbourhood of the equilibrium spacing the NaCl molecule is predominantly ionic. If one tries to extend this ionic description to infinite internuclear distance, the molecule would dissociate to Na^+ and Cl^- ions. The sum of the total energies of the isolated ions, however, is higher than that of the neutral atoms. Within the adiabatic approximation to the motion of the nuclei [7] one has to expect crossing between the potential curves for the ionic and covalent state. The change from the ionic model at small distances to the atomic model at large distances makes alkali halides interesting systems for a discussion of the dissociation limit.

2. Statistical Total Energy of the Separated Constituents

In the statistical $X\alpha$ -method it is possible to use non-integer orbital occupation numbers [5]. Defining $0 < x < 1$ as the ionicity and $E_{\text{Cl}}(x)$ as the statistical total energy of a Chlorine ion Cl^{-x} with the configuration $1s^2 2s^2 2p^6 3s^2 3p^{5+x}$ and concomitantly $E_{\text{Na}}(-x)$ to be the statistical total energy of the corresponding Sodium ion Na^x with configuration $1s^2 2s^2 2p^6 3s^{1-x}$, the statistical total energy of the separated constituents (i.e. for the internuclear distance $R = \infty$) $E(\infty, x)$ is the sum of these two energies

$$E(\infty, x) = E_{\text{Cl}}(x) + E_{\text{Na}}(-x). \quad (1)$$

The minimum of $E(\infty, x)$ with respect to x , $\frac{\partial E(\infty, x)}{\partial x} = 0$, implies that

$$\frac{\partial E_{\text{Cl}}(x)}{\partial x} = - \frac{\partial E_{\text{Na}}(-x)}{\partial x} \quad (2)$$

Since in the $X\alpha$ -model the derivative of the total energy with respect to the orbital occupation number is the corresponding orbital energy, $\frac{\partial E_{\text{Cl}}(x)}{\partial x}$ is the $3p$ orbital energy of a Chlorine ion of ionicity x and $-\frac{\partial E_{\text{Na}}(-x)}{\partial x}$ the $3s$ orbital energy of the

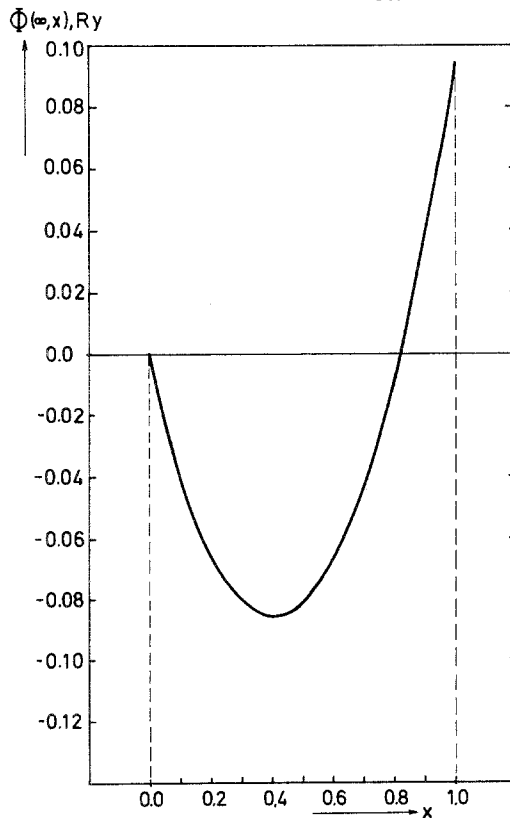


Fig. 1. Variation of $\Phi(\infty, x) = E(\infty, x) - E(\infty, 0)$ with respect to x , $E(\infty, x)$ being the total energy of separated ions of ionicity x [Eq. (1)]

corresponding Sodium ion. The minimum of $E(\infty, x)$ refers exactly to that ionicity, where a Chlorine and Sodium ion have equal top valence orbital energies (Fermi-Dirac statistics) [5].

Figure 1 shows the variation of the quantity $\Phi(\infty, x) = E(\infty, x) - E(\infty, 0)$ with respect to x , where $E(\infty, 0)$ is the sum of the statistical total energies of the free neutral atoms Sodium and Chlorine. In Fig. 2 the corresponding orbital energies are plotted versus the ionicity. Implying Fermi-Dirac statistics to the limit of the separated constituents, an ionicity x_0 of 0.405, i.e. $\text{Na}^{+0.405}$ and $\text{Cl}^{-0.405}$, and an partially ionic reference value of $\Phi(\infty, x_0) = -0.086 \text{ Ry}$ (-1.1696 eV) has to be encountered.

3. The Ionic and Covalent State of Sodium Chloride

Three different sets of orbital occupation numbers have been investigated: namely $K|8\sigma^2 3\pi^4 9\sigma^0|$, the ionic state; $K|8\sigma^1 3\pi^4 9\sigma^1|$, the covalent state and the transition state $K|8\sigma^{1.5} 3\pi^4 9\sigma^{0.5}|$, with K being $|1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 6\sigma^2 2\pi^4 7\sigma^2|$.

In all cases atomic exchange parameters [8] (α_{vt}) have been used within the atomic spheres and a mean value of these ($\alpha = 0.7268$) for all other regions of space.

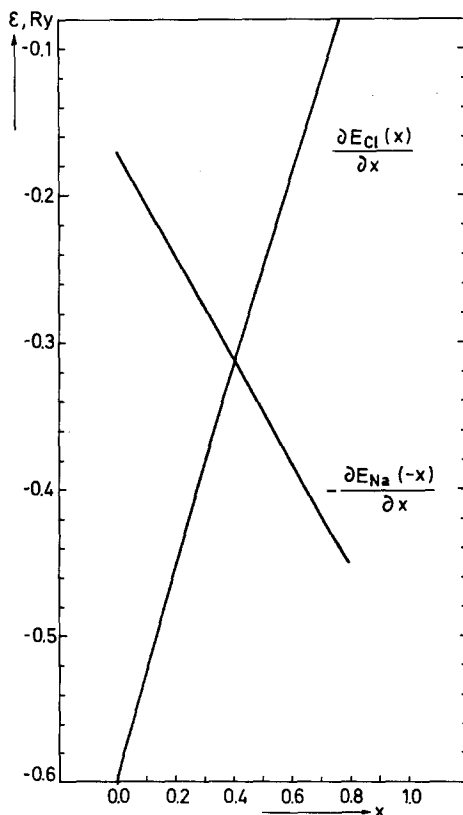


Fig. 2. Variation of the top valence orbital energies for Sodium, $-\frac{\partial E_{\text{Na}}(-x)}{\partial x}$, and for Chlorine, $\frac{\partial E_{\text{Cl}}(x)}{\partial x}$, with respect to the ionicity x

According to Slater's transition state concept [5], the difference of the statistical total energies for the ionic state, $E^{\text{IS}}(R)$, and the covalent state, $E^{\text{CS}}(R)$, at a given internuclear separation R can be approximated very efficiently by the transition energy $\bar{\epsilon}(R)$,

$$\begin{aligned}\bar{\epsilon}(R) &= E^{\text{IS}}(R) - E^{\text{CS}}(R) \\ \bar{\epsilon}(R) &= \epsilon_{8\sigma}(R) - \epsilon_{9\sigma}(R),\end{aligned}\quad (3)$$

where $\epsilon_{8\sigma}(R)$ and $\epsilon_{9\sigma}(R)$ are the 8σ - and 9σ -molecular orbital energies at a particular internuclear distance R for the state $K|8\sigma^{1.5}3\pi^49\sigma^{0.5}|$. In order to illustrate this approximation, the corresponding quantities at $R=6$ a.u. are cited, namely $E^{\text{IS}}(R) - E^{\text{CS}}(R) = -0.369$ Ry and $\bar{\epsilon}(R) = -0.365$ Ry.

In the atomic X α calculation the statistical total energy for the free Chlorine ion, $E_{\text{Cl}}(1)$, can only be extrapolated, because the $3p$ orbital energy would be positive for $x=1$ (Fig. 2). Therefore similar difficulties have to be expected for the potential curve of the ionic state for medium and large values of R due to the 8σ and 3π orbital energies. In order to avoid such difficulties, $E^{\text{IS}}(R)$ is computed directly only for $R < 7$, while for $R > 7$ $E^{\text{CS}}(R)$ is evaluated. The respective quantities are obtained by means of the transition state concept, according to (3).

4. Computational Aspects

Atomic sphere radii R_p are chosen to be half of the internuclear distance. Unfortunately, because of numerical difficulties, it is not possible to enlarge the Chlorine sphere radius arbitrarily. However, up to a value of $R=9$, sphere radii

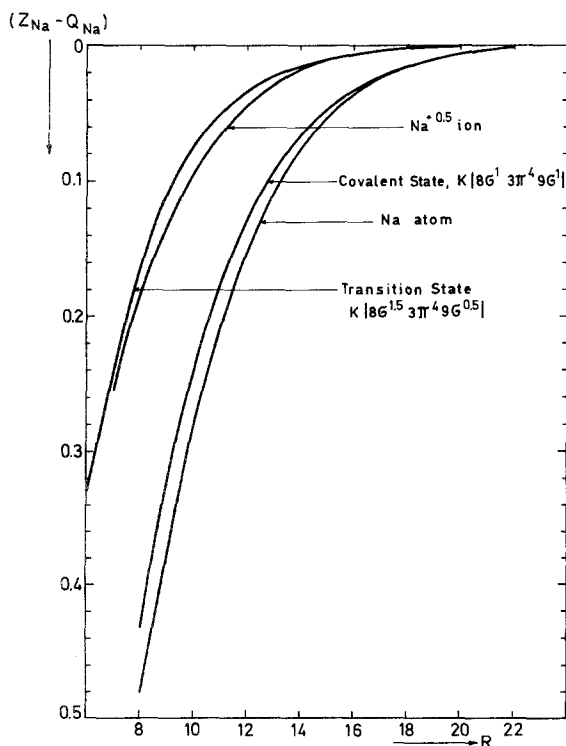


Fig. 3. Comparison of the quantities $[Z_{\text{Na}} - Q_{\text{Na}}^{\text{at}}(R)]$ and $[Z_{\text{Na}} - Q_{\text{Na}}^{\text{mol}}(R)]$ for Sodium, plotted versus the internuclear distance R (a.u.)

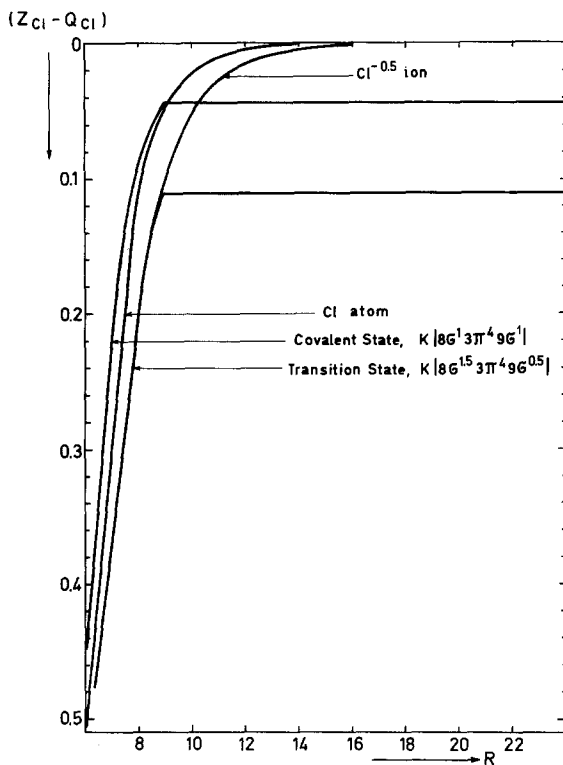


Fig. 4. Comparison of the quantities $[Z_{Cl} - Q_{Cl}^{at}(R)]$ and $[Z_{Cl} - Q_{Cl}^{Mol}(R)]$ for Chlorine, plotted versus the internuclear distance R (a.u.)

can be chosen to be $R/2$, whereas for all $R > 9$, a constant value of 4.5 is used for the Chlorine sphere and $R/2$ for the Sodium sphere radius.

In order to discuss this numerical deficiency, the quantities $[Z_p - Q_p^{at}(R)]$, Z_p being the atomic number and $Q_p^{at}(R)$ being the radial integral of the spherical symmetric charge density in the range $[0, R/2]$ for the atomic system p , are compared in Figs. 3 and 4 with the corresponding molecular quantities $[Z_p - Q_p^{Mol}(R)]$, with $Q_p^{Mol}(R)$ being the radial integral of the spherical symmetrical charge density in sphere p in the range $[0, R_p]$. Figure 3 shows the comparison for the Sodium constituent, for which no restrictions to the sphere radius are necessary. This figure indicates that for large values of R corresponding curves eventually coincide and that for medium large R for both, the covalent state and the transition state, the "ionicity" of the Sodium sphere $[Z_{Na} - Q_{Na}^{Mol}(R)]$ will be less positive as compared to the respective atomic value. Figure 4 shows quite drastically the effect of the restriction to the Chlorine sphere radius. For the covalent, as well as for the transition state, the proper decay of the quantity $[Z_{Cl} - Q_{Cl}^{Mol}(R)]$ for $R > 9$ is disrupted. The comparison with the corresponding atomic cases shows that the "ionicity" of the Sodium and Chlorine sphere for these values of R will be essentially the same as in the atomic systems. Since in the case of the covalent state this deficiency is quite small and since the main goal is to calculate the statistical total energy, the results will be essentially unaffected by this restriction to the Chlorine sphere radius. For example, for $R = 10.0$ a.u. the statistical total energy is changed

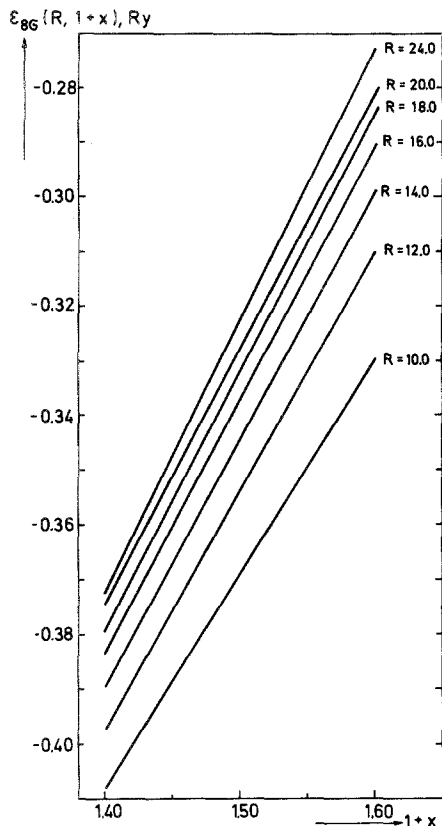


Fig. 5. Variation of the 8σ -orbital energy, $\varepsilon_{8\sigma}(R, 1+x)$, corresponding to states $K[8\sigma^{1+x}3\pi^49\sigma^{1-x}]$, with respect to its occupation number $(1+x)$ for a selection of medium and large internuclear distances R (a.u.)

only within the self-consistent threshold, increasing the Chlorine sphere radius from 4.5 to 4.8.

For the transition state this restriction is more critical. Similarly to the atomic case (Fig. 2) for the $3p$ orbital energy the value of the 8σ - and 3π -orbital energy will be effectively changed by the "ionicity" of the Chlorine sphere. In Fig. 5 the energy of the 8σ -orbital, $\varepsilon_{8\sigma}(R, 1+x)$, corresponding to states $K[8\sigma^{1+x}3\pi^49\sigma^{1-x}]$, is plotted versus its occupation number $(1+x)$ for medium and large values of R . Utilizing the essentially linear dependence of the 8σ -orbital energy with respect to its occupation number, one can effectively correct the value at $x = 0.5$ by means of atomic quantities $[Z_{\text{Cl}} - Q_{\text{Cl}}^{\text{at}}(R)]$ and the "ionicity" of the Chlorine sphere in the molecule. The slope $K(R)$ of the 8σ -orbital as a function of its occupation number $(1+x)$, is given by

$$K(R) = \frac{\varepsilon_{8\sigma}(R, 1+x) - \varepsilon_{8\sigma}(R, 1+x_0)}{x - x_0} \quad (4)$$

The correction for the "ionicity" of the Cl-sphere can be set up as:

$$\Delta Q(R) = [Q_{\text{Cl}}^{\text{at}}(R) - Q_{\text{Cl}}^{\text{Mol}}(R)] \quad (5)$$

where $\Delta Q(R)$ is the approximate for the missing charge arising from the 3π - and 8σ -orbital, when restricting the Chlorine sphere radius to 4.5 for $R > 9$.

Since in the R range, where corrections are necessary, the 3π - and 8σ -orbital energies are degenerated and have the same slope with respect to a variation of the corresponding occupation number, one has to correct both orbital energies simultaneously in order not to destroy this degeneracy. For this reason the transition energy is reformulated in the following manner,

$$\begin{aligned}\bar{\epsilon}(R) &= \frac{1}{2}[\epsilon_{8\sigma}(R) + \epsilon_{3\pi}(R)] - \epsilon_{9\sigma}(R) \\ &= \frac{1}{2}[\epsilon_{8\sigma}^0(R) + \epsilon_{3\pi}^0(R) + K(R)\Delta Q(R)] - \epsilon_{9\sigma}(R) \\ &= \epsilon_{8\sigma}^0(R) + \frac{1}{2}K(R)\Delta Q(R) - \epsilon_{9\sigma}(R) = \epsilon_{8\sigma}(R) - \epsilon_{9\sigma}(R),\end{aligned}\quad (6)$$

where $\epsilon_{8\sigma}^0(R)$ is the 8σ -orbital energy for $x = 0.5$ as calculated with the restriction to the Chlorine sphere radius. $\epsilon_{8\sigma}(R)$ is the corrected value.

5. Results

In Fig. 6 the values of $\epsilon_{8\sigma}^0(R)$, $\epsilon_{8\sigma}(R)$, and $\epsilon_{9\sigma}(R)$ are plotted together with the transition energy $\bar{\epsilon}(R)$ and the uncorrected transition energy $\bar{\epsilon}^0(R) = \epsilon_{8\sigma}^0(R) - \epsilon_{9\sigma}(R)$

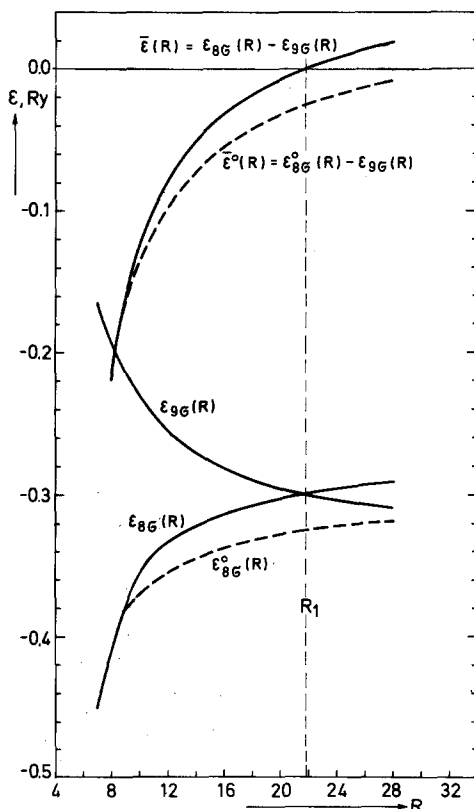


Fig. 6. The orbital energies $\epsilon_{8\sigma}(R)$, $\epsilon_{8\sigma}^0(R)$ and $\epsilon_{9\sigma}(R)$ for the transition state and the transition energies $\bar{\epsilon}(R)$ and $\bar{\epsilon}^0(R)$ are plotted versus the internuclear distances (a.u.). The zero location of $\bar{\epsilon}(R)$ is denoted by R_1

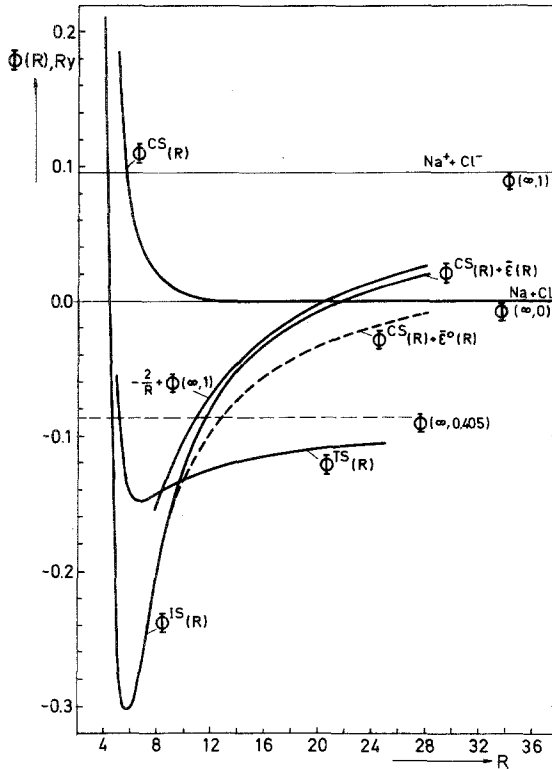


Fig. 7. Potential curves for the covalent state $\Phi^{\text{CS}}(R)$, the ionic state $\Phi^{\text{IS}}(R)$, and the transition state $\Phi^{\text{TS}}(R)$. $\Phi^{\text{CS}}(R) + \bar{\epsilon}(R)$ is the corrected potential curve for the ionic state, when using the transition energy $\bar{\epsilon}(R)$ for $R > 9$, whereas $\Phi^{\text{CS}}(R) + \bar{\epsilon}^0(R)$ is the uncorrected potential curve. The reference level for the separated partial ions of ionicity $x = 0.405$ is denoted by $\Phi(\infty, 0.405)$

versus the internuclear separation. The crossing of the two orbital energy curves $\epsilon_{8\sigma}(R)$ and $\epsilon_{9\sigma}(R)$, i.e. the zero location of the function $\bar{\epsilon}(R)$ refers exactly to that value of R , where the covalent and the ionic state will have equal statistical total energies. In Fig. 7 the potential curves for the covalent and the ionic state with reference to the statistical total energy $E(\infty, 0)$ of the free neutral atoms, $\Phi^{\text{IS}}(R)$ and $\Phi^{\text{CS}}(R)$, and the classical Coulomb potential $-2/R + \Phi(\infty, 1)$ are plotted versus R . In the same figure the potential curve $\Phi^{\text{TS}}(R)$ for the transition state $K|8\sigma^{1.5} 3\pi^4 9\sigma^{0.5}|$ is shown with reference to the limit of the free neutral atoms. The attractive branch of this potential curve is almost exactly of the form $-2/Rx^2 + \Phi(\infty, x)$ with x being 0.5, indicating a dissociation of partial ions with ionicity 0.5.

Calculated results for the ionic state predict an equilibrium separation R_0 of 5.6 a.u. and a dissociation energy D_e with respect to the free neutral atoms of 4.12 eV. R_0 is about 18% larger than the experimental value of 4.74 a.u. [7, 9], the calculated dissociation energy differs only by 3.5% from the experimental value (4.27 eV) [7, 9]. The crossing of the potential curves for the covalent and the ionic state is about $R_1 = 21.6$ a.u., whereas the classical Coulomb potential, $-2/R + \Phi(\infty, 1)$, predicts crossing at 20.7 a.u. The calculated crossing point and dissociation energy D_e are therefore quite satisfactory.

6. Discussion

The potential curve for the covalent state predicts no minimum at all, and is for all values of $R > 12a$ a straight horizontal line. The calculated dissociation energy and especially the equilibrium separation for the ionic state suffer to some extent from the muffin tin approximation, since for $R < 6$ a considerable amount of charge is located in the region of the flat portion of the muffin tin potential. But at least, as compared with similar calculations for covalent molecules [2,3] the effect is much less drastical.

As one can see from Fig. 7, a self-consistent approach does not automatically provide the minimum of the statistical total energy with respect to the Fermi-Dirac constraint. Just as in the case of transition metal atoms [10], one has to vary the occupation numbers of partially filled orbitals in separate calculations in order to get the most favourable state according to Fermi-Dirac statistics. For this state the top valence orbitals will be degenerate. In Fig. 8 the value of x for which $\varepsilon_{8\sigma}(R, 1+x) = \varepsilon_{9\sigma}(R, 1-x)$, is plotted versus the internuclear separation R . This function $x = x(R)$ is 1 at about $R = 8$, has the value 0.5 at R_1 , the internuclear separation of the crossing, and approaches the Fermi-Dirac value 0.405 from above. In other words for all values of $R < 8$ the 9σ -orbital is unoccupied and therefore the NaCl molecule will be ionic. For all values of $R > 8$ the NaCl molecule will be a closed shell system.

Constraining results to Fermi-Dirac statistics, one does not get free neutral atoms, but partial ions. The dissociation energy with respect to the Fermi-Dirac

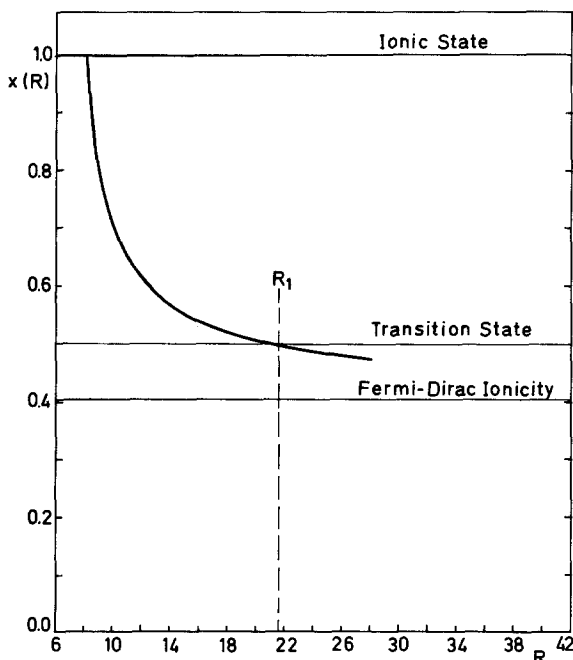


Fig. 8. The value of $x(R)$, for which the 8σ -orbital energy $\varepsilon_{8\sigma}(R, 1+x)$ and the 9σ -orbital energy $\varepsilon_{9\sigma}(R, 1-x)$ are degenerate. ($1 \pm x$) being the corresponding occupation number, $x(R)$ is plotted as a function of the internuclear distance R (a.u.). R_1 denotes the value of R for which crossing of the potential curves for the ionic and covalent state occurs

limit, $\Phi(\infty, 0.405)$, would be rather poor, namely 2.95 eV, which is only about 69% of the experimental value. Using the x -values in Fig. 8 to compute a ground state with respect to Fermi-Dirac statistics, one gets a smooth potential curve, showing no crossing at all, leading from the pure ionic state to separated partial ions of ionicity 0.405.

Restricting the characterization of states of molecules to sets of integer occupation numbers, the adiabatic dissociation process of the NaCl system yields free atoms as the most favourable end channel products. Calculations with integer occupation numbers show a distinct crossing of the potential curves for the covalent and the ionic state; the crossing itself being basically an artifact of the adiabatic motion of nuclei.

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