I. SOME DETAILS OF TRANSFORMING SCHRÖDINGER EQUATION TO ALGEBRAIC EQUATIONS

In the main text, we have shown that the Schrödinger equation for $\psi$ can be transformed into the following equations for $M$ and $N$,

\[
\left[(1 - \eta^2) \frac{d^2}{d\eta^2} - 2(|m| + 1)\eta \frac{d}{d\eta} - \frac{1}{2} \tilde{E} R^2 \eta^2 - R(Z_1 - Z_2)\eta - A\right] M(\eta) = 0, \tag{S1}
\]

\[
\left[(\xi^2 - 1) \frac{d^2}{d\xi^2} + 2(|m| + 1)\xi \frac{d}{d\xi} + \frac{1}{2} \tilde{E} R^2 \xi^2 + R(Z_1 + Z_2)\xi + A\right] N(\xi) = 0. \tag{S2}
\]
For the ground state, $M(\eta) = C_1 e^{\beta_1(\eta)}$, $N(\xi) = C_2 e^{\beta_2(\xi)}$ and $m = 0$. The resulting equations for $\beta_1$ and $\beta_2$ read

\[
(1 - \eta^2) \frac{d^2 \beta_1}{d\eta^2} + (1 - \eta^2) \left( \frac{d\beta_1}{d\eta} \right)^2 - 2\eta \frac{d\beta_1}{d\eta} - \frac{1}{2} \tilde{E} R^2 \eta^2 - R(Z_1 - Z_2) \eta - A = 0, \tag{S3}
\]

\[
(\xi^2 - 1) \frac{d^2 \beta_2}{d\xi^2} + (\xi^2 - 1) \left( \frac{d\beta_2}{d\xi} \right)^2 + 2\xi \frac{d\beta_2}{d\xi} + \frac{1}{2} \tilde{E} R^2 \xi^2 + R(Z_1 + Z_2) \xi + A = 0. \tag{S4}
\]

In deriving Eq. (S3), we have used $\frac{dM}{M d\eta} = \frac{d\beta_1}{d\eta}$ and $\frac{d^2 M}{M d\eta^2} = \frac{d^2 \beta_1}{d\eta^2} + \left( \frac{d\beta_1}{d\eta} \right)^2$. One can use similar relations to derive Eq. (S4). Denoting $u = \frac{d\beta_1}{d\eta}$ and $v = \frac{d\beta_2}{d\xi}$, Eqs. (S3) and (S4) reduce to the Riccati equations as presented in the main text. Compared with the Schrödinger equation, the Riccati equations reduce a 2nd-order ODE to two 1st-order ODEs at the sacrifice of linearity of the equation. Furthermore, by introducing $q = 1 - \frac{1}{\xi}$, the Riccati equations can be cast into the following forms:

\[
f_1(\eta) \frac{du}{d\eta} + f_2(\eta) u^2 + f_3(\eta) u + f_4(\eta, A, \tilde{E}) = 0, \tag{S5}
\]

\[
g_1(q) \frac{dv}{dq} + g_2(q) v^2 + g_3(q) v + g_4(q, A, \tilde{E}) = 0. \tag{S6}
\]

Here $f_1 = f_2 = 1 - \eta^2$, $f_3 = -2\eta$, $f_4 = -\frac{1}{2} \tilde{E} R^2 \eta^2 - R(Z_1 - Z_2) \eta - A$; $g_1 = (2 - q)(1 - q)^2 q$, $g_2 = (2 - q)q$, $g_3 = 2(1 - q)$, $g_4 = \frac{R^2}{2} \tilde{E} + R(Z_1 + Z_2)(1 - q) + A(1 - q)^2$. One can see that $f_i$’s and $g_i$’s are polynomials of $\eta$ and $q$, i.e., $f_i = \sum_j f^i_j \eta^j$ and $g_i = \sum_j g^i_j q^j$. With the Taylor expansion of $u(\eta) = \sum_{k=0}^\infty u_k \eta^k$ and $v(q) = \sum_{k=0}^\infty v_k q^k$, one can compare the $\eta^{k-1}$ ($k \geq 1$) terms in Eq. (S5) and $q^k$ terms in Eq. (S6), which lead to

\[
\sum_{l=0}^{k-1} (k - l) f^1_l u_{k-l} + \sum_{l=0}^{k-1} f^2_l \sum_{i=0}^{k-1} u_i u_{l-i} + \sum_{l=0}^{k-1} f^3_l u_{k-1-l} + f^4_{k-1} = 0, \tag{S7}
\]

\[
\sum_{l=1}^{k} (k + 1 - l) g^1_l v_{k+1-l} + \sum_{l=1}^{k} g^2_l \sum_{i=0}^{k-l} v_i v_{l-i} + \sum_{l=0}^{k} g^3_l v_{k-l} + g^4_k = 0. \tag{S8}
\]

In deriving Eq. (S8), we have used $g^0_1 = g^0_2 = 0$. Solving for $u_k$ and $v_k$ in Eq. (S7) and Eq. (S8) leads to the following recursive relations:

\[
u_k = -\frac{1}{k^2 f^2_1} \left[ \sum_{l=1}^{k} (k - l) f^1_l u_{k-l} + \sum_{l=0}^{k-1} f^2_l \sum_{i=0}^{k-1} u_i u_{l-i} + \sum_{l=0}^{k-1} f^3_l u_{k-1-l} + f^4_{k-1} \right], \tag{S9}
\]

\[
v_k = -\frac{1}{kg^1_1 + g^2_0} \left[ \sum_{l=2}^{k+1} (k + 1 - l) g^1_l u_{k+1-l} + \sum_{l=1}^{k} g^2_l \sum_{i=0}^{k-l} v_i v_{l-i} + \sum_{l=1}^{k} g^3_l v_{k-l} + g^4_k \right], \tag{S10}
\]
by which each \( u_k \) or \( v_k \) becomes a function of four unknowns, \( u_0, v_0, \tilde{E}, A \). To determine these unknowns, we invoke the boundary conditions at \( \eta = \pm 1, q = 0 \) and 1:

\[
\begin{align*}
-2u(1) - \frac{1}{2} \tilde{E}R^2 - R(Z_1 - Z_2) - A &= 0, \quad (S11) \\
2u(-1) - \frac{1}{2} \tilde{E}R^2 + R(Z_1 - Z_2) - A &= 0, \quad (S12) \\
2v(0) + \frac{1}{2} \tilde{E}R^2 + R(Z_1 + Z_2) + A &= 0, \quad (S13) \\
v(1)^2 + \frac{1}{2} \tilde{E}R^2 &= 0. \quad (S14)
\end{align*}
\]

Here we have been assumed that \( u, v \) and their derivatives are finite. By Eq. (S13), we can solve \( v_0 = v(0) = -\frac{\tilde{E}R^2}{4} - \frac{R(Z_1 + Z_2)}{2} - \frac{A}{2} \), reducing the number of unknowns to 3. Then the remaining three equations can be written as correlated algebraic equations of \( u_0, \tilde{E} \) and \( A \) once we plug in the Taylor expansion formula of \( u \) and \( v \) at the boundary points. Truncating the Taylor series to finite order, i.e., considering only finite number of \( u_k \)'s and \( v_l \)'s, Eqs. (S11), (S12) and (S14) can be solved by the standard multi-dimensional Newton’s iteration approach. [1] Although with a given truncation length, there could exist multiple solutions, one can find a unique convergent series when enlarging the truncation length, and the exact \( A, \tilde{E} \) and \( u_0 \) are given by this limiting solution.

**II. SOME DETAILS OF THE RICCATI EQUATIONS FOR EXCITED STATES**

For a generic state, the Riccati equations are given by

\[
\begin{align*}
\left[ (1 - \eta^2) \frac{d^2}{d\eta^2} - 2(|m| + 1)\eta \frac{d}{d\eta} - \frac{1}{2} \tilde{E}R^2 \eta^2 - R(Z_1 - Z_2)\eta - A \right] M(\eta) &= 0, \quad (S15) \\
\left[ (\xi^2 - 1) \frac{d^2}{d\xi^2} + 2(|m| + 1)\xi \frac{d}{d\xi} + \frac{1}{2} \tilde{E}R^2 \xi^2 + R(Z_1 + Z_2)\xi + A \right] N(\xi) &= 0. \quad (S16)
\end{align*}
\]

Assuming finite derivatives at the nodes of the wave functions, one can write \( M(\eta) = P(\eta)e^{\beta_1(\eta)} \) and \( N(\xi) = Q(\xi)e^{\beta_2(\xi)} \), where \( P(\eta) = \prod_{l=1}^{L}(\eta - a_l) \) and \( Q(\xi) = \prod_{k=1}^{K}(\xi - b_k) \). Here \( L \) and \( K \) are the number of nodal points of \( M(\eta) \) and \( N(\xi) \), respectively. Substituting these exponential expressions into Eq. (S15) and Eq. (S16) and after simplification, we arrive
Here we have denoted $u = \frac{d\eta}{d\xi}$, $v = \frac{d^2\eta}{d\xi^2}$. Next, we introduce $q = 1 - \frac{1}{\xi}$ in Eq. (S18) to transform the domain of $\xi$ into a finite interval $[0, 1]$. The resulting equation reads

$$S_0(q)q(2-q)(1-q)^2\frac{dv}{dq} + S_0(q)q(2-q)v^2 + 2(1-q)\left[(m+1)S_0(q) + S_1(q)q(2-q)\right]v + S_0(q)\left[\frac{1}{2} \tilde{E} R^2 + R(Z_1 + Z_2)(1-q) + A(1-q)^2\right] + (1-q)^2\left[2(m+1)S_1(q) + S_2(q)q(2-q)\right] = 0.$$  

(S19)

Here $S_0(q) = \prod_{i=1}^{K}[1 - b_i(1-q)]$, $S_1(q) = \sum_{i=1}^{K} \prod_{j\neq i}[1 - b_j(1-q)]$, $S_2(q) = \sum_{i=1}^{K} \sum_{j\neq i} \prod_{k\neq i,k\neq j}[1 - b_k(1-q)]$. Eq. (S17) and Eq. (S19) can be solved analogously as for the ground state; here one shall treat each node ($a_l$ or $b_k$) as an additional variable, and introduce a nodal condition accordingly by plugging $\eta = a_l$ or $\xi = b_k$ into the formulas.

### III. SOME DETAILS OF MOBIUS TRANSFORMATION AND DETERMINATION OF COEFFICIENTS

In some cases $u(\eta)$ has singularities in the unit circle on the complex plane so that our Taylor expansion is no longer valid on the entire domain of $[0, 1)$. Then we shall move these singularities outside the unit circle through a Mobius transformation as has been practiced in Ref. [2]. Since this transformation is valid only for variables defined on $[0, 1]$, it cannot be applied directly to our $\eta$, which is defined on $[-1, 1]$. Then our solution is to decompose $u(\eta)$ into an even and an odd function of $\eta$, $u(\eta) = s(p) + 2\eta w(p)$ with $p = \eta^2$. The resulting ODEs for $s(p)$ and $w(p)$, deducible from Eq. (S17), become coupled equations. Take the
ground state for an example, they read

\[ 2(1 - p) \frac{ds}{dp} + 4(1 - p)s w - 2s - R(Z_1 - Z_2) = 0, \]  
\[ 4p(1 - p) \frac{dw}{dp} + 4p(1 - p)w^2 + 2(1 - 3p)w - \left( \frac{1}{2} \hat{E} R^2 p + A \right) + (1 - p)s^2 = 0. \]

Eqs. (S20) and (S21) are equivalent to Eq. (S5). By choosing proper parameter \( t > 0 \), one

\[ p' = \frac{p(1 + t^2)}{p + t^2}. \]

Then performing Taylor expansion in terms of \( p' \), we have convergent series \( s = \sum_{k=0}^{\infty} s_k (p')^k \) and \( w = \sum_{k=0}^{\infty} w_k (p')^k \) in the unit circle. Transforming \( p' \) back into \( \eta \), we can obtain the

\[ \beta_1 = c_1 \eta + c_2 \eta^2 + c_3 \arctan \left( \frac{\eta}{t} \right) + c_4 \ln(\eta^2 + t^2) + \sum_{j=1}^{\infty} c_{5+j} \eta \left( \frac{t^2}{\eta^2 + t^2} \right)^j + \sum_{j=1}^{\infty} c_{6+j} \left( \frac{t^2}{\eta^2 + t^2} \right)^j. \]

Here \( c_1 = \sum_{k=0}^{\infty} s_k (1 + t^2)^k, c_2 = \sum_{k=0}^{\infty} w_k (1 + t^2)^k, c_3 = t \sum_{k=0}^{\infty} s_k (1 + t^2)^k \sum_{j=1}^{k} \frac{(-1)^j k!}{j!(k-j)!} (2j-3)! \]
\[ c_4 = -t^2 \sum_{k=0}^{\infty} k w_k (1 + t^2)^k, c_{5+j} = \sum_{k=j+1}^{\infty} s_k (1 + t^2)^k \sum_{i=j+1}^{k} \frac{(-1)^i k!}{i!(k-i)!} (2i-3)! \]
\[ c_{6+j} = t^2 \sum_{k=j+1}^{\infty} w_k (1 + t^2)^k \frac{k!(-1)^k}{j!(j+1)!(k-j-1)!}. \]

We can further separate a linear term from \( \beta_1 \), i.e.,

\[ \beta_1(\eta) = -\alpha_1 \eta + F_1(\eta). \]

Then \( \alpha_1 = -u(\eta)|_{\eta=0} = -u_0 = -s_0 \), and

\[ F_1 = (c_1 - s_0) \eta + c_2 \eta^2 + c_3 \arctan \left( \frac{\eta}{t} \right) + c_4 \ln(\eta^2 + t^2) \]
\[ + \sum_{j=1}^{\infty} c_{5+j} \left( \frac{t^2}{\eta^2 + t^2} \right)^j \eta + \sum_{j=1}^{\infty} c_{6+j} \left( \frac{t^2}{\eta^2 + t^2} \right)^j. \]

Since \( \beta_1 \) and \( \alpha_1 \) are \( t \)-invariant, \( F_1 \) must also be \( t \)-invariant even though its definition formally involves \( t \).

For some excited states, singularities of \( v(q) \) can also arise in the unit circle of the \( q \) plane
when \( R \) is small. Then we can introduce anotherMobius transformation for \( q \),

\[ q' = \frac{q}{1 - d + dq}, \]

where \( d \in [0, 1) \) is a parameter. Expanding \( v \) into a Taylor series of \( q' \) leads to a convergent
series in the unit circle, \( v = \sum_{k=0}^{\infty} v_k(q')^k \). Then transforming \( q' \) back into \( \xi \) and integrating

S5
over \( \xi \), we obtain the formula for \( \beta_2 \) as

\[
\beta_2 = \int_\xi^\infty v(\xi')d\xi' \nonumber
\]

\[
= \sum_{k=0}^\infty v_k \int_\xi^\infty \left(1 - \frac{1 - d}{\xi' - d}\right)^k d\xi' \nonumber
\]

\[
= \sum_{k=0}^\infty v_k \left[\xi - k(1 - d) \ln(\xi - d) + \sum_{j=2}^k \frac{(-1)^j k!}{j! (k-j)!} \int_\xi^\infty \left(1 - \frac{d}{\xi' - d}\right)^j d\xi'\right] \nonumber
\]

\[
= \sum_{k=0}^\infty v_k \left[\xi - k(1 - d) \ln(\xi - d) - (1 - d) \sum_{j=2}^k \frac{(-1)^j k!}{j! (k-j)!} \left(1 - \frac{d}{\xi - d}\right)^{j-1}\right] \nonumber
\]

\[
= \sum_{k=0}^\infty v_k \left[\xi - k(1 - d) \ln(\xi - d) + (1 - d) \sum_{j=1}^{k-1} \frac{(-1)^j k!}{j! (j+1)! (k-j-1)!} \left(1 - \frac{d}{\xi - d}\right)^j\right]. \quad \text{(S26)}
\]

To recast Eq. (S26) as

\[
\beta_2 = -\alpha_2 \xi + \gamma \ln \xi + F_2(\xi), \quad \text{(S27)}
\]

we define \( \alpha_2 = -\sum_{k=0}^\infty v_k \), \( \gamma = -(1 - d) \sum_{k=0}^\infty kv_k \), \( F_2(\xi) = \gamma \ln \left(\frac{\xi - d}{\xi}\right) + (1 - d) \sum_{k=2}^\infty v_k h_k \left(\frac{1-d}{\xi - d}\right) \) with \( h_k(x) = \sum_{j=1}^{k-1} \frac{(-1)^j k!}{j! (j+1)! (k-j-1)!} x^j \). \( \alpha_2 \) and \( \gamma \) can be further simplified using the following relations,

\[
\alpha_2 = -v|_{q'=1} = -v|_{q=1}, \quad \text{(S28)}
\]

\[
\gamma = -(1 - d) \frac{dv}{dq}|_{q'=1} = -\frac{dv}{dq}|_{q=1}. \quad \text{(S29)}
\]

Setting \( q = 1 \) in Eq. (S19) and the derivative of Eq. (S19), we have

\[
\alpha_2^2 + \frac{1}{2} \tilde{E} R^2 = 0, \quad \text{(S30)}
\]

\[
2\alpha_2 \gamma + 2(K + m + 1) \alpha_2 - R(Z_1 + Z_2) = 0, \quad \text{(S31)}
\]

by which we can solve \( \alpha_2 = \sqrt{-\frac{1}{2} \tilde{E} R^2} \) and \( \gamma = \frac{R(Z_1 + Z_2)}{2\alpha_2} - (K + m + 1) \). \( \alpha_2 \) and \( \gamma \) are apparently \( d \)-invariant. Then it follows that \( F_2 \) is also \( d \)-invariant although it formally involves \( d \). In the special choice of \( d = 0 \), one recovers the expression in the main text.

Table S1 summarizes \( \tilde{E} \), \( \alpha_1 \), \( \alpha_2 \) and \( \gamma \) for the ground state in the limit \( R \to 0 \) and \( R \to \infty \).

IV. DETAILS OF FEW-PARAMETER GROUND STATE VARIATIONAL SOLUTIONS

The exact ground state wave function is given by a product of a power prefactor, an exponentially decaying term modulated by an \( F \) function. Inspired by this form, a simple
Table S1: Limiting behaviors of $\tilde{E}$, $\alpha_1$, $\alpha_2$ and $\gamma$ for the ground state. When $Z_1 = Z_2$, $\alpha_1$ is strictly 0 for any $R$, which is not shown in the table.

| Term          | $R \to 0$          | $R \to \infty$ |
|---------------|---------------------|-----------------|
| $E$           | $-(Z_1 + Z_2)^2/2$  | $-Z_1^2/2$      |
| $\alpha_2/R$ | $(Z_1 + Z_2)/2$     | $Z_1/2$         |
| $\gamma$     | 0                   | $Z_2/Z_1$       |
| $\alpha_1/R$ | $Z_1/2$             | $Z_1/2$         |

trial wave function for variational approximation is to neglect the modulator,

$$\psi_{V3} = \xi^{\lambda_1} \exp(-\lambda_2 \xi - \lambda_3 \eta), \quad \text{(S32)}$$

where the subscript “$V3$” indicates the number of variational parameters. The resulting estimate for the energy is given by the minimizer of the variational formula $E = \langle \psi | \hat{H} | \psi \rangle / \langle \psi | \psi \rangle$ with respect to $\lambda_i$'s. Improvement over this energy can be achieved by approximating the modulator by simple elementary functions that leads to the correct asymptotic behavior, giving rise to 4-parameter trial wave functions:

$$\psi_{V4} = \xi^{\lambda_1} \exp(-\lambda_2 \xi - \lambda_3 \eta) \cosh(\lambda_4 \eta), \quad \text{(S33)}$$

$$\psi_{V4'} = \xi^{\lambda_1} \exp(-\lambda_2 \xi - \lambda_3 \eta) \exp(\lambda_4 \eta^2). \quad \text{(S34)}$$

In particular, the modulator has been approximated by $\ln \cosh(\lambda_4 \eta)$ and $\lambda_4 \eta^2$, respectively.

In Figure S1, we compare variational results with the exact ground state energy curve for $H_2^+$ and $\text{HeH}^{2+}$. Here (and also in the main text) the exact energy curve is accurate to $10^{-10}$ Hartree. For $H_2^+$, $\lambda_3$ is strictly zero by symmetry, thus reducing the number of variational parameters to 3 even though it is under the name of “$V4$”. As shown in Figure S1(a)(b), scheme ”$V4$” performs the best among the schemes tested, whose error is on the magnitude of $10^{-4}$ Hartree, while scheme ”$V3$” gives a qualitatively wrong energy curve because of the unphysical plateau in the wave function. This shows the necessity of the modulator function. For $\text{HeH}^{2+}$, to demonstrate the necessity of splitting the term $-\alpha_1 \eta$ from $\beta_1$, we also consider the following 2-parameter trial wave function,

$$\psi_{V2} = \xi^{\lambda_1} \exp(-\lambda_2 \xi), \quad \text{(S35)}$$

As shown in Figure S1(c)(d), here scheme ”$V3$” is sufficient to yield an accurate enough energy curve, while scheme ”$V2$” gives qualitatively wrong energy because of an unphysical plateau in the wave function.
Figure S1: (a) Variational energy curves for $H_2^+$. The blue and the black line almost overlap each other, and their difference is shown in the inset. (b) Variational wave functions for stretching $H_2^+$. Here the nuclei are placed at $(0, 0, \frac{R}{2})$ and $(0, 0, -\frac{R}{2})$, where $R = 1, 2$ and 5 Bohr are shown in black, red and blue, respectively. The dotted and the dash-dot curve overlap with the solid line in most of the domain. (c) Variational energy curves for $\text{HeH}^2+$. The red and the blue curve almost overlap with the exact curve, with their difference shown in the inset. (d) Variational wave functions for stretching $\text{HeH}^2+$. Colors refer to the same as in (b). The dashed, the dotted and the solid line overlap in most of the domain.

In summary, one can construct trial wave functions with as few as 3 parameters that give accurate ground state energy and wave function.

V. SOME SUPPLEMENTAL RESULTS

A. Evolution of MOs and their nodal surfaces as bond is stretched

As the Schrödinger equation of a single-electron diatomic molecule is separable, the wave function can be factorized into $M(\eta)$, $N(\xi)$, and $e^{\pm i n \phi}$. This suggests that a nodal surface of the wave function must correspond to a node of either $M(\eta)$ or $N(\xi)$. Then by solving
Figure S2: Contour plots of $2s\sigma$ wave function for HeH$^{2+}$ with (a) $R = 5$ Bohr, (b) $R = 10$ Bohr, and (c) $R = \infty$. Here (a) and (b) are calculated by our method, and (c) is calculated by $\frac{1}{\sqrt{2}}(\psi_{2s,\text{He}} + \psi_{2p_{z},\text{He}})$ with $\psi_{2s,\text{He}}$ and $\psi_{2p_{z},\text{He}}$ being the atomic orbitals of He. We have set the $z$-axis as the bonding axis and placed the helium nucleus at $z = 0$. The nodal surfaces have been highlighted by the red lines. As $R$ increases, the nodal surface (which is an ellipsoid) gradually enlarges its radius of curvature near the helium position and expands its encircled region until becoming a paraboloid when $R = \infty$, which is nothing but the nodal surface of the $sp$ hybrid atomic orbital of He.

for the roots of these functions, we end up with $\eta = \eta_0$ or $\xi = \xi_0$ for some $\eta_0$ and $\xi_0$. By definition, such nodal surfaces are hyperboloids or ellipsoids. To see how such nodal surfaces evolve into the nodal surfaces of atomic orbitals in the dissociation limit, particularly for a heteronuclear diatomic molecular ion, we illustrate in Figure S2 using the example of $2s\sigma$ orbital of HeH$^{2+}$ for increasing $R$. It is worth noticing that the $2s\sigma$ molecular orbital reduces to the $sp$ hybrid atomic orbital rather than pure $2s$ or $2p$ orbital of He. This is reasonable because $2s$ and $2p$ orbitals of He become degenerate in the infinite nuclear separation. Such hybridization also occurs for homonuclear molecules such as H$_2^+$, see Figure 4 of the main text.

B. Computational advantage of our method over LCAO expansion

We have shown in the main text that the conventional basis expansion methods cannot capture the nodal surface shapes even qualitatively with commonly used basis sets. Here we further demonstrate that our method can achieve greater accuracy with much smaller
Computational cost. As shown in Figure S3(a), for the ground state of H$_2^+$ with bond length of chemical interest ($R < 8$ Bohr), our solution gives very accurate energy (for most cases error less than $10^{-7}$ Hartree) with a total number of 60 $u_k$’s and $v_k$’s [3]. This is several orders of magnitude better than the aug-cc-pV5Z results with 160 basis functions. In fact, one has to use an unprecedentedly large Gaussian basis set to reach our accuracy, as one can estimate from the error trend when enlarging basis set. Similar situation is also observed for heteronuclear molecules such as HeH$^{2+}$, see Figure S3(b). Furthermore, we have found that our computational advantage is even more pronounced for excited states. For example, for the 2$s\sigma$ state of H$_2^+$, we can achieve much better accuracy than Gaussian basis set with as few as 30 $u_k$’s and $v_k$’s, as shown in Figure S4.

C. Some additional analysis on the modulator function

The number of $u_k$’s or $v_k$’s (let us call them cut-offs here) needed for an accurate evaluation of the wave function and modulator function are determined by converging the total energy to a given threshold (set to $10^{-10}$ Hartree in the present work). For chemically interesting $R$ (typically within 10 Bohr for the ground state, could be larger for excited states), a cut-off of less than 50 is sufficient in most cases. For example, a cut-off of 20 is sufficient to give
Figure S4: (a) Comparing computational efficiency between conventional basis expansion (computed with pySCF) and our method, as indicated by their energy error for the excited 2sσ state of H₂⁺ for a chemically interesting range of R. Note that the basis expansion results have a spurious avoided crossing in the range of R = 3.5 – 4.5 Bohr where a nonadiabatic transition takes place between 2sσ and 3dσ. To make a fair comparison, here we show the diabatic curves with 2sσ symmetry for regions away from the nonadiabatic transition. (b) Comparing the exact energy curves of 2sσ and 3dσ states with the basis expansion results (using aug-cc-pV5Z as basis), which have a spurious avoided crossing. [4]

accurate modulator functions for HeH²⁺, see Figure S5 for an illustration. For larger R, however, the cut-off (especially for uₖ) grows with R. For example, 500 uₖ’s are needed for R = 50 Bohr. Yet such large R is of little significance for chemical problems.

In our previous work on 1D H₂⁺ with soft Coulomb potential, we have obtained the exact analytical ground state wave function for the following Schrödinger equation: \(-\frac{1}{2} \frac{d^2 \phi}{dx^2} + v_R(x)\phi + \frac{1}{\sqrt{a^2 + R^2}} \phi = E\phi\), where \(v_R(x) = -\frac{1}{\sqrt{a^2 + (x-\frac{1}{2}R)^2}} - \frac{1}{\sqrt{a^2 + (x+\frac{1}{2}R)^2}}\). [2] Here we compare our 3D results with 1D particularly for the modulator function \(F\). Note that \(F\) is a single-variable function of \(\lambda = 1 - \sqrt{\frac{4x_0^2 + R^2}{y}}\) in 1D, where \(y = \sqrt{a^2 + (x + R/2)^2} + \sqrt{a^2 + (x - R/2)^2}\) is analogous to our \(R\xi\) in 3D. [2] To make an easy comparison, here we reduce \(F(\xi, \eta)\) also to a single-variable function by plotting it along a line parallel to the bonding axis with distance \(x_0\) and parametrizing this line by \(\lambda = 1 - \frac{\sqrt{4x_0^2 + R^2}}{R\xi}\), in analogy to that in 1D.

The comparison is shown in Figure S6. As can be seen, the overall trend is similar in 1D and 3D; \(F\) is a mildly varying function of \(\lambda\) for small \(R\) and grows rapidly in the small-\(\lambda\) region for large \(R\). This validates that our 1D model of H₂⁺ captures the essential 3D physics during molecular dissociation. Although \(F\) is a decreasing function in 1D but not in 3D for small \(R\), this is largely due to the artifact of the soft Coulomb potential and only of minor
importance.

Figure S5: $F_1(\eta)$ and $F_2(\xi)$ for HeH$^{2+}$ calculated with different cut-offs (numbers of $u_k$’s for $F_1$ and numbers of $v_k$’s for $F_2$). Here $R = 0.5$ Bohr for (a) and (b); and $R = 5$ Bohr for (c) and (d). The exact curves are obtained using sufficiently large number (100) of $u_k$’s and $v_k$’s.
Figure S6: Comparing modulator $F$ of $\text{H}_2^+$ with different bond length $R$ (in unit of Bohr) as a function of $\lambda$ for 3D (solid lines) and 1D with soft Coulomb potential (dashed lines). For the 3D case, $F$ is plotted along a line parallel to the bonding axis with distance $x_0 = 1$ Bohr; for the 1D case, the soft Coulomb parameter is $\alpha = 1$ Bohr. We have shifted each curve here such that $F$ is zero when $\lambda = 0$. 
References

(1) Ng, S.; Lee, Y. Variable dimension Newton-Raphson method. *IEEE Trans. Circuits Syst. I, Fundam. Theory Appl.* 2000, 47, 809–817.
(2) Li, C. Exact analytical ground state solution of 1D $H_2^+$ with soft Coulomb potential. *J. Math. Chem.* 2022, 60, 184–194.
(3) When Mobius transformation is needed, the number of $u_k$’s and $v_k$’s turns into the total number of expansion coefficients of the transformed functions (where $u_k$’s reduce to $w_k$’s and $s_k$’s).
(4) Hatton, G. J. The noncrossing rule and spurious avoided crossings. *Phys. Rev. A* 1976, 14, 901–910.